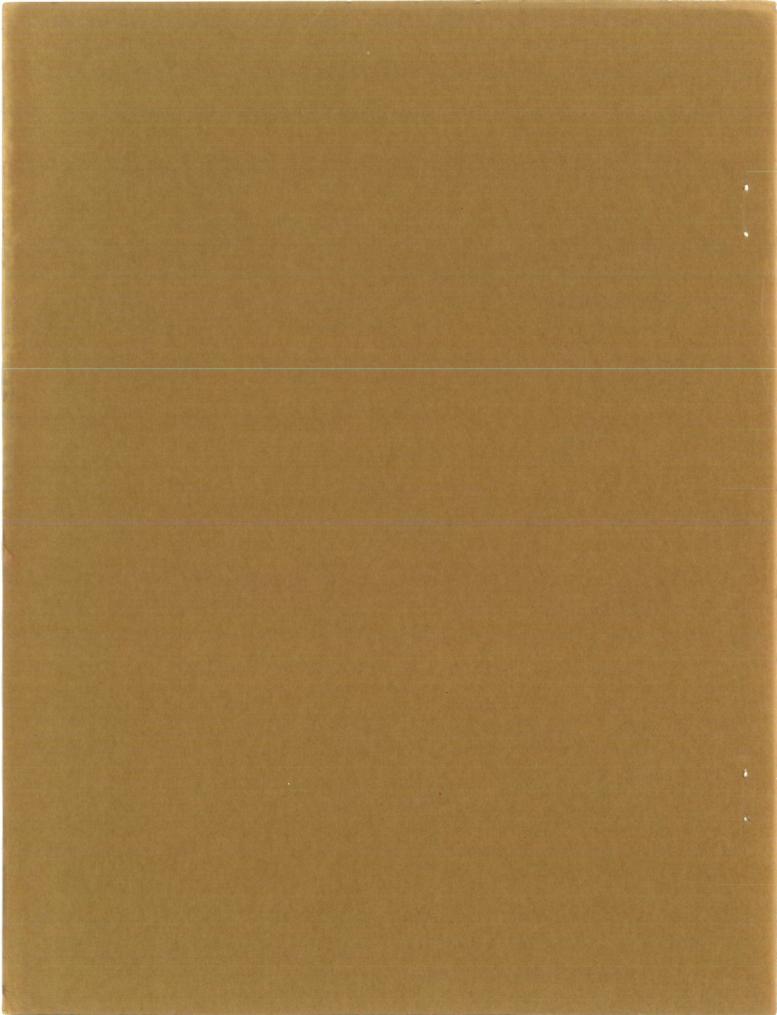
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POTENTIAL OF HEAVY-MINERAL-BEARING ALLUVIAL DEPOSITS IN THE PACIFIC NORTHWEST

BY A. J. KAUFFMAN, JR., AND K. D. BABER

=United States Department of the Interior — December 1956



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SUMMARY

The alluvial deposits of the Pacific Northwest have been investigated and worked with varying degrees of intensity since about the middle of the 19th century. Earlier efforts, of course, were centered about the placer-gold content of the deposits; later, the Oregon beach sands were exploited for their chrome content, and, still more recently, deposits in Idaho were worked for their content of monazite, a rare-earth mineral which also contains significant quantities of thorium.

The composition of alluvial deposits seems to depend mainly upon the nature of the source rock from which the detrital material was derived and upon the resistance of the individual mineral grains to the agencies of weathering and transportation. The processes of crushing and concentration used in ore dressing are applied in a leisurely but nonetheless effective manner when exposed rock masses are eroded by natural forces. Weathering effects a continuous disintegration and chemical decomposition, wherein resistant minerals are set free as individual grains and new minerals are formed. Erosion carries these detrital products down the slopes into natural waterways, where a mechanical separation of heavy particles from light is accomplished by the running water. The accumulation of such resistant, heavy particles through the ages has resulted in formation of the black-sand deposits. In addition to the associated gangue minerals, heavy sand deposits in the Pacific Northwest may contain the following constituents of possible economic value: Gold, platinum, chromite, ilmenite, magnetite, garnet, zircon, monazite, columbite-tantalite, and radioactive blacks.

Development of a stable and profitable placer-mining industry must of necessity be based upon the content of heavy minerals having economic value and also on the present and foreseeable future demands for the recovered product. The alluvial deposits in the area with which this report is concerned contain recoverable quantities of chromite, ilmenite, magnetite, zircon, monazite, columbite-tantalite, and radio-active blacks. Chromite, and columbite-tantalite and the radioactive blacks are being recovered from deposits in Oregon and Idaho, respectively. Monazite-dredging activities have ceased, at least temporarily, in Idaho. At the present time there is no ready market for the ilmenite, magnetite, and zircon. The high freight structure makes it difficult for titanium- and zirconium-bearing concentrates from Idaho, for example, to compete in eastern markets. Utilization of these heavy minerals very likely will depend upon the establishment of an industry within a reasonable radius of the deposits.

INTRODUCTION

Metallurgical research and development over the past quarter century and particularly during the past decade have focused attention on many relatively unfamiliar elements. The stimulation of a major world conflict, the international race for atomic supremacy, and the expanding field of electronics have contributed to this interest, and the group of elements variously referred to as minor, rare, and uncommon has taken on new significance. Because of these advances in the knowledge of

and military and industrial applications for the rare-earth metals, thorium, titanium, zirconium, hafnium, columbium (niobium), tantalum, as well as uranium, in the past few years, this report deals primarily with the Idaho alluvial sand deposits; other Pacific Northwest alluvial deposits are treated in a less complete manner.

A recognition of the need for extensive exploration projects to evaluate known deposits and to locate new occurrences has resulted from Government and industrial research leading to wider application of these metals. For many years, dredging of alluvial deposits (both beach and stream placers) for gold and, in some instances, platinum has been an important phase of the mining industry in the Pacific Northwest. Associated with the precious metals in many of these deposits is a relatively low concentration of what commonly are called "heavy minerals." Because many of the minerals in this fraction are dark in color, such occurrences are referred to as "black sand" deposits. More recently the term "radioactive blacks" has been applied to certain of the constituents that contain, in addition to columbium and tantalum, uranium, thorium, and certain rare earths and cannot be classified accurately without a detailed examination. In most instances little or no interest was shown in these heavy minerals, and no attempts were made to recover them. Their presence was a source of annoyance to operators because the high specific gravity of these minerals caused them to interfere with full recovery of gold values.

The Idaho alluvial sand deposits first promised to support a mineral industry about the turn of the century. Interest was centered about the thorium content of the sands because of the popular use of thoria-impregnated mantles for lighting with gas. However, the relative inaccessibility of the Idaho deposits at that time, combined with competition from eastern and foreign sources producing for a manipulated market, made economic exploitation virtually impossible, and there was little activity until 1950.

The advent of atomic energy, with research that over the years brought to light new and increasingly important uses for the rare-earth and columbium-tantalum as well as the thorium content of the alluvial sands, again directed attention to the Idaho deposits. Government support programs based on the thorium content of these sands made possible rebirth of an alluvial sand industry in Idaho. Present advanced technology can make available to the Nation's defense and industrial establishments not only the thorium and rare earths but also the columbium and tantalum and the titanium and zirconium content of the deposits. These latter two in recent years have assumed increasingly greater significance as strategic and special-use industrial metals.

ACKNOWLEDGMENTS

The authors are indebted to Prof. J. S. Walton, Chemical Engineering Department, Oregon State College, Corvallis, Oreg., for assembling portions of the basic material used in this report, and to E. J. Carlson, formerly a commodity specialist, Branch of Rare and Precious Metals, Division of Minerals, Bureau of Mines, Washington, D. C., for supplying data on analyses of domestic monazite samples.

HISTORICAL BACKGROUND

Gold reportedly was discovered in the Pacific Northwest as early as 1845, but significant placer occurrences were not found until 1852. Immediately thereafter many important strikes were made, and placer mining boomed until about 1870. No mention of the other heavy minerals found in the alluvial deposits seems to have

been made until 1896, when Lindgren $(\underline{1})^{\underline{3}/}$ reported the occurrence of monazite in the Idaho Basin, Boise County, Idaho. In the eastern part of the country at that time, monazite recovery from placer deposits was beginning on a small scale. This new industry was destined to thrive until 1911.

In an attempt to determine whether the alluvial deposits of the Western States contained useful minerals in addition to monazite, the Geological Survey began an investigation of the black sands occurring on the Pacific slope. The results of this survey were published in 1905. (2) A concentration plant was set up in Portland, Oreg., by the Geological Survey and during 1905 and 1906 thousands of samples were examined and analyzed. Black sands containing chromite, ilmenite, magnetite, zircon, garnet, and monazite (not all of the minerals in every deposit) were found in 14 counties in Idaho; 13 counties in Oregon; and 3 counties each in Montana and Washington.

During the latter part of 1905 magnetite concentrates from a deposit near Astoria, Oreg., were smelted in an electric arc furnace set up at the plant in Portland. (3) The first 2 runs yielded a total of 90 pounds of metal from 300 pounds of concentrates. Interest fostered by the survey prompted the Centerville Mining & Milling Co. to begin mining operations in the Boise Basin, Idaho. Several tons of monazite concentrates were produced but not sold because of unfavorable prices. The plant was destroyed by a forest fire in 1910.(4) During the early years of World War II chromite was recovered from the coast of southwest Oregon. Subsequently, zircon recovered as a byproduct from this operation was used by the Bureau of Mines staff at Albany, Oreg., in the original research that resulted in development of the magnesium-reduction process (Kroll process) for producing ductile zirconium metal. The first sustained placer dredging in the Pacific Northwest (for other than precious metals) began in January 1951 after an intensive search by the Bureau of Mines under contract to the Atomic Energy Commission indicated minable quantities of monazite. A gold dredge modified to recover all of the heavy minerals was put into operation on Big Creek near Cascade, Valley County, Idaho. Production continued until about the middle of 1955, when monazite-dredging operations ceased. A deposit in the Bear Valley area, Valley County, is being worked for columbitetantalite and radioactive black minerals.

Near Coquille in Coos County, Oreg., chromite concentrates produced during World War II are being reworked before being processed to ferrochrome at a plant near Spokane, Wash. It is planned to work other deposits in the vicinity when the stockpiled material is exhausted. At another location in Coos County, an acid-leaching plant has been constructed to upgrade chromite concentrates derived from the beach sands to make them acceptable for delivery to the GSA purchase depot at Grants Pass, Oreg.

The reader is invited to consult the following references for a comprehensive review of the history of monazite activities in the Pacific Northwest as well as elsewhere in the country. $(5\ 6\ 7\ 8\ 9\ 10\ 11\ 12\ 13)$

COMPOSITION

It may be of interest to consider estimates that have been made for the elemental composition of the earth's crust. Brian Mason in his "Principles of Geochemistry" sets forth estimates based upon data developed by Goldschmidt and Clark. Only

^{3/} Underlined numbers in parentheses refer to citations in the references at the end of this report.

8 elements are present in the earth's crust in quantities greater than 1 percent. These elements - oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium - compose almost 99 percent of the total. This means that copper, lead, and zinc plus all of the other well-known as well as less familiar elements compose about 1 percent of the earth's crust. The group of metals that will be covered in this report represents less than 0.5 percent of the total.

Titanium, the most abundant element in the group, is present in concentrations of about 0.440 percent.

Zirconium (0.0220 percent) is present in the earth's crust in higher concentrations than chromium, and greater than copper, lead, and zinc combined.

As a group, the rare-earth metals (0.0151 percent) equal vanadium and zinc and are greater than nickel, tungsten, and tin.

Columbium and tantalum combined (0.0026 percent) are found in concentrations greater than cobalt, lead, molybdenum, and arsenic.

Thorium (0.0012 percent) is about 3 times more plentiful than uranium.

The potentially commercial constituents of the alluvial deposits in the Pacific Northwest that will be included in this report are chromite, ilmenite, zircon, monazite, columbite-tantalite, and radioactive blacks.

Chromite, a combination of the oxides of chromium, iron, and additional other elements, occurs in peridotite and derived serpentine and is found as a constituent of black-sand deposits. Chromium in various forms has a widespread use in the metallurgical, chemical, and refractory industries. Although domestic chromite requirements are met almost entirely by imports, the Oregon alluvial deposits constitute a sizable reserve of subgrade material.

Ilmenite, a titanium-bearing mineral present in large proportions in most black sands of this area, cannot compete at present with rutile and eastern ilmenite for the production of titanium metal or pigment. However, recent application of the metal and its alloys to various specialized military uses has made it reasonable to believe that it may become more important to the Nation's defense establishment. Some ilmenites contain small quantities of columbium and tantalum.

Zircon, a silicate of zirconium, occurs in varying quantities in the gravels of the Northwest and may become a useful byproduct of dredging operations, although competition from Florida and foreign sources may impair its status as a valuable product. Zirconium, like titanium, has found many new applications in recent years; the most important of these makes use of its high corrosion resistance, combined with its ability to pass slow neutrons, an attribute that makes it extremely valuable in the nuclear-energy field.

Monazite is disseminated widely as an accessory mineral in igneous and metamorphic rocks and, as a detrital product of the weathering and wearing of these rocks, is often found in beds of streams that rise in or pass through such formations. Beaches are another common location for the accumulation of monazite as a decomposition product of the parent rock. Chemically, monazite is a thorium-bearing

phosphate of the 15 rare-earth elements. Usually it contains iron, magnesium, aluminum, zirconium, manganese, beryllium, and other elements in small and varying amounts in substitution for the rare earths. Small percentages of uranium are found occasionally in some monazites.

In addition to monazite, bastnaesite (fluocarbonate of the rare-earth metals) is an important commercial source mineral of the rare-earth metals.

Columbium-tantalum minerals, present in small proportions in some placers, are in relatively short supply in the United States and elsewhere throughout the world. Columbite and tantalite, the most abundant and widespread of the naturally occurring minerals of columbium and tantalum, are oxides of these elements, as are the less common radioactive blacks - euxenite, fergusonite, and samarskite. These minerals are found in granite pegmatites and in detrital deposits; columbite and tantalite usually contain iron and manganese, while euxenite, fergusonite, and samarskite contain yttrium, certain rare-earth elements, and sometimes thorium and uranium. Titanium is also a constituent of euxenite and samarskite.

Because of the widespread distribution of granite pegmatites with different geologic environment and because the alluvial deposits from this source are formed in diverse ways, it would be expected that not only would the proportions of one mineral to another vary but also within any one mineral there would be extreme variations in the proportions of the several elements. This is true. In one monazite the thorium content may exceed 10 percent, while in another it may be 1 percent or less; in columbite-tantalite minerals the columbium-tantalum ratio usually varies also and all the other common constituents of black sands are subject to these same variations. An extremely complicated cooccurrence situation thus exists, and it is beyond the scope of this paper to attempt to explain geologic phenomena related to chemical composition and mode of occurrence of alluvial sands.

Rare earths are important and valuable constituents of monazite, and in most pure monazite their oxides will constitute 56 to 68 percent, by weight, of the mineral. Since thorium occurs as a substitution element for rare-earth elements with the phosphate radical, it follows that, when the thorium content is high, the rare-earth-element percentage will be lower correspondingly. The same is true of uranium; and, for monazites over the world, a convenient rule of thumb is that the sum of the rare-earth oxides plus the thorium oxide and uranium oxide will equal 68 to 69 percent of the monazite weight. Some deviations will occur from this loose rule, but in most instances it is a convenient approximation.

It is important to know the chemical composition of the mineral because, as pointed out above, this may vary widely, not only in rare-earth content but also in distribution of individual rare-earth elements. More analytical work has been done on the sands from the Big Creek placer in the Long Valley district of Idaho than on any other deposits because it is the source of most of the monazite production from Idaho to date. The heavy minerals from a group of drill holes were concentrated and assayed for ThO_2 and U_3O_8 ; selected grains of monazite from the same holes also were assayed. The results are given in table 1. Table 2 lists ThO_2 and U_3O_8 analyses for selected monazite grains from deposits throughout the United States.

TABLE 1. - Analyses of black-sand concentrates and selected grains of monazite from drill hole samples - Big Creek placer

	ThO2, percent		U308, percent		Monazite in
	In	In	In	In	sand (calculated)
Sample No.	sand	monazite	sand	monazite	percent <u>1</u> /
1	0.240		0.012		6.2
2	.277		.011		6.9
3	.258	4.12	.011	0.139	6.5
4	.254	4.23	.009	.132	6.2
5	.274		.010		6.7
6	.487	4.18	.014	.132	11.6

1/ Taking into account radiometric analyses.

TABLE 2. - Analyses of domestic monazites by
Bureau of Mines laboratories

			Chemical	
	Location		perc	ent
Deposit	County	State	U308	ThO2
Alexander Flats	Elmore	Idaho	0.18	5.98
Bear Valley	Valley	do.	.27	4.82
Big Creek	do.	do.	.13	4.20
Boise Basin	Boise	do.	.10	3.20
Clear Creek	Valley	do.	.12	4.13
Corral Creek	do.	do.	.10	4.39
Gold Fork	do.	do.	.18	4.84
Horsethief Basin	do.	do.	.11	4.74
Mud Flats	Ada	do.	.22	6.24
Rabbit Creek	Boise	do.	.36	5.50
Scott Valley	Valley	do.	.17	4.11
Secesh Meadows	Idaho	do.	.25	5.75
Valley Creek	Custer	do.	.18	3.31
Warren Meadows	Idaho	do.	.17	3.96
Victor Area	Ravalli	Montana	.52	6.00
Trail Creek	Beaverhead	do.	.10	4.10
Deadwood Formation $\frac{1}{2}$	Sheridan	Wyoming	.12	8.80
Lemhi Lode 2/	Lemhi	Idaho	.003	.85
Pecos Lode $\frac{2}{}$	San Miguel	New Mexico	.34	9.86
Broad River	Cherokee	South Carolina	.58	4.64
Buffalo Creek	Cleveland	North Carolina	.49	6.55
Duncan Creek	do.	do.	.62	6.66
First Broad River	do.	do.	.50	5.91
Hollow Creek	Aiken	South Carolina	•54	5.08
Horse Creek	do.	do.	.51	5.07
Knob Creek	Cleveland	North Carolina	.42	7.28
Pacolet River	Spartanburg	South Carolina	.67	5.26
Sandy Run Creek	Rutherford	North Carolina	.80	4.63
South Muddy Creek	McDowe11	do.	.36	4.30
Silver Creek	Burke	do.	.44	4.80
Ward Creek	Cleveland	do.	.76	5.94
1/ Sandstone conglomera	±0			

1/ Sandstone conglomerate.

 $\overline{2}$ / Vein deposit.

OCCURRENCES AND RESERVES

Idaho

In Idaho the heavy sands are distributed in three areas: (1) The western part of the State, where the drainage passes through the Idaho batholith; (2) the eastern part of the State, where drainage passes through the Belt Rocks; and (3) the Snake River deposits.

The largest known deposits of black sands rich in monazite in the United States are in central Idaho in an area bounded on the north by the Salmon River and on the south by the Boise River, with the west boundary a few miles past the town of Cascade and the east boundary continuing approximately due south from the confluence of the Salmon River and the South Fork. Outside this large general area are many other placer gravels that may have good possibilities for industrial development. The Snake River from American Falls to Hells Canyon contains gold-bearing black sands, some of which have been exploited in earlier years (12). Dredging permits have been issued for use on the Snake River from Weiser downstream to Hells Canyon, with the possibility that a distance of 100 miles downstream from Weiser might show profitable operation when the gold values, as well as the other black-sand constituents, are considered.

The more important alluvial deposits in the Pacific Northwest are listed, by counties, in table 3. A consideration of many of these deposits follows.

Valley County (Western Portion)

The Long Valley district has witnessed the only large-scale commercial monazite operations to date in Idaho and, for that matter, in the United States. It comprises an area 20 miles long, enclosing the North Fork of the Payette River and ranging in width from 10 miles at the north to about 0.5 mile at the south.

TABLE 3. - Summary of alluvial deposits in Idaho by county location

County	Includes -
Valley County (western portion)	Big Creek, Corral Creek, Clear Creek, Pearsol Creek, Scott Valley, Horsethief Basin, Beaver Creek, West Mountain, and Gold Fork deposits.
Valley County (central portion)	Upper Bear Valley, Middle Bear Valley, Elk Creek, White Hawk Basin, and Stolle Meadows deposits.
Boise County	Boise Basin, Moores Creek, Summit Flats, and Garden Valley deposits.
Idaho County(southern portion)	Warren Meadows, Secesh Meadows, Ruby Meadows, Lake Creek, and Kelley Meadows deposits.

Principal activity has been centered in the Big Creek area. In January 1951 Baumhoff-Marshall, Inc., began operating a 6-foot Yuba dredge. Later the same year Idaho-Canadian Dredging Co. put a similar-size dredge in operation, and Warren Dredging Corp. started with a 4-foot boat in the same general area. These operations ceased, at least temporarily, about the middle of 1955.

Corral Creek and Pearsol Creek placers are promising sources of monazite under existing conditions.

Scott Valley, Beaver Creek, and Horsethief Basin placers are regarded at present as marginal as far as monazite is concerned but could be worked profitably if more gold and radioactive blacks are found than is expected at present.

Clear Creek and Gold Fork deposits probably cannot be worked profitably for monazite unless the price is at least doubled (emergency conditions).

The weight of evidence is that the alluvial gravels in this general area were derived from the higher granite terrane east of the river valleys, where the monazite and associated minerals were distributed widely and sparsely in the source rock. By weathering and fluvial action they have become concentrated in lakes, stream beds, or both, with the probability that each sometimes alternated in forming the gravel and sand beds. Depths of the deposits vary widely, but there are indications that certain deposits may extend downward some hundreds of feet. Too little drilling has been done to determine depths over most of the area. A drilling program to evaluate further the extent of the deposits represents an objective which clearly should be undertaken.

Valley County (Central Portion)

In the Bear Valley area of the upper reaches of the Middle Fork of the Salmon River are found relatively large quantities of radioactive blacks but less monazite. The middle section of the valley probably is marginal in content of these minerals. Porter Bros. Corp. is now operating in Bear Valley.

Boise County

The earliest known monazite activity in Idaho was near Centerville in the Boise Basin. The thorium oxide content of the monazite was greater than 5 percent. Boise Basin deposits are marginal for monazite but might be exploited if larger quantities of radioactive blacks and gold were found.

Garden Valley placers probably could not be operated profitably for monazite unless there was a substantial price increase. Preliminary studies indicate the presence of columbite-tantalite and radioactive blacks.

Idaho County

Secesh Meadows has monazite, radioactive blacks, and gold in quantities that make it a reasonably good mining prospect.

Ruby Meadows is marginal for monazite but might be exploited profitably if larger quantities of radioactive blacks and gold were found. The K & D Mining Co. has operated a bucketline dredge in this area.

Warren Meadows probably could not be operated profitably for monazite unless the price is increased substantially.

Placers along the South Fork of the Clearwater River near Elk City contain radioactive blacks, and in some areas scheelite is found as a constituent of the sands.

Elmore County

The Dismal Swamp placer on the Middle Fork of the Boise River is rather small but contains a relatively large percentage of columbite-tantalite, with smaller quantities of zircon, radioactive blacks, monazite, and gold.

Lemhi County

Massive monazite occurs in a deposit between Shoup and Gibbonsville. Examination of the occurrence indicates a width of 5 to 30 feet, with exposures over a distance of about 800 feet. No depth data are available. There are many placers in the county, some of which contain radioactive blacks.

A report and map issued by the Idaho Bureau of Mines and Geology include localities and data on the origin of the black-sand deposits in the State (14).

Reserves of ilmenite in Idaho have been estimated to exceed 3 million tons. Ilmenite from the Big Creek deposit collected as a byproduct of the monazite-concentration operation at Boise since 1950 totaled, at cessation of operations, about 80,000 tons. As it stands, it will average about 45 percent TiO₂ and by rerunning can be raised to about 52 percent TiO₂, which compares favorably with the ilmenite now being used at Sorel, Canada, to make titanium slag for sale to the United States. Assuming a 60-percent chemical recovery of titanium dioxide from the 45 percent now present in the stockpile, there is available approximately 22,000 tons of recoverable titanium dioxide containing about 13,000 tons of titanium metal. An additional 65,000 tons of metal is potentially available from an estimated 400,000 tons of ilmenite in the Big Creek deposit. If the same percentages are taken to apply to all of the ilmenite in the area, the titanium-metal content reaches a total of more than 500,000 tons.

Indications are that, in the listed placers, there are 120,000 tons of zircon, which, if again taken at 60-percent chemical recovery after processing, represents 35,000 tons of zirconium metal.

Data on reserves of monazite and the radioactive blacks cannot be released.

Garnet is present in large quantities compared with the demand for it; and conversely, magnetite, though large in tonnage compared to monazite, is small in tonnage compared with United States annual iron-ore consumption.

While in Idaho there is no currently active market for these products, except in small quantities, combined they represent potentially valuable materials that might make economic the mining of those locations that are now marginal or unprofitable.

As more field work is done by men trained in exploration, there is little doubt that more reserves similar to those now known will be found. A Bureau of Mines report (15) describes about 90 placer areas in Lemhi County alone. The Snake River channel is known to contain black sands and gold over much of its length in Idaho. It is unlikely that the reserves located in the future will be richer than those of Big Creek or Pearsol Creek because Bureau of Mines personnel sought out the most promising black-sand sources, as indicated by earlier investigations. However, with increased emphasis on the need for columbium-tantalum minerals and the radioactive blacks, some of the known deposits, hitherto not examined carefully for these latter constituents, might prove more favorable than earlier consideration has indicated.

Montana

Monazite, columbite-tantalite, and radioactive blacks are known to occur in pegmatites and heavy sand deposits. Day and Richards (2) mention monazite occurrences in Granite and Ravalli Counties. In Flathead County the Trail Creek and Bighole River placers are believed by Sterrett (8) to be extensions of the Idaho deposits. Recent field work by the Bureau of Mines has resulted in locating two fairly large deposits in the area.

Thorite has been reported to occur in a deposit near Norris, Madison County.

Heinrich $(\underline{16})$ discusses the pegmatitic occurrence of columbium-tantalum minerals and the rare earths in Montana. He also lists a number of occurrences, mostly in massive deposits but with specific mention of placers in the general area of Lake Delmo and the head of California Gulch near Laurin, Madison County.

Up to the present, the most promising Montana black-sand deposits found containing monazite or the columbium-tantalum-thorium elements have been those in the Victor area and at Trail Creek, but the possibility of future findings should not be excluded for either massive or placer deposits.

Oregon and Washington

Elsewhere in the Northwest there are no known large deposits of monazite-bearing sands. There are extensive deposits of beach sands in Oregon and Washington; but, so far as has been determined, these sands contain only small quantities of monazite with larger proportions of chromite, zircon, ilmenite, and garnet. Day and Richards (2) list the mineral composition of more than 200 black sands from Oregon and Washington with monazite appearing in only a few of these samples. According to Pardee (17), samples from Coos Bay and Yaquina Bay contained noteworthy amounts of zircon, and a little monazite was found in several samples mostly from Clatsop County.

A Bureau of Mines report $(\underline{18})$ on Oregon beach sands was issued in 1942. Hundhausen $(\underline{19})$, in 1947, writing on the chromiferous sand deposits in the Coos Bay area, omits any mention of monazite as a constituent of the Oregon beach sands. The report describes chromite mining in the Coos Bay region during World War II and gives data on the quantities of chromite, ilmenite, zircon, garnet, and magnetite that were produced. With regard to the reserve potential of the Oregon beach sands, the coastal black-sand deposits contain 2 to 8 percent Cr_2O_3 and can be beneficiated to yield an estimated 250,000 tons of Cr_2O_3 in a 40-percent concentrate.

From this consideration of the occurrences of alluvial deposits in the Pacific Northwest, it appears that the reserves of monazite and radioactive blacks in Idaho are far larger than in any other State in the area, although the possibility remains that additional quantities may be found in Montana. There is little likelihood that similar deposits in Oregon and Washington will figure prominently in the production of these minerals. The potentiality of chromite, ilmenite, and zircon from the various deposits as marketable products for a locally situated industry, however, must not be forgotten. To evaluate alluvial deposits properly, an energetic and systematic program must be followed that includes drilling and petrographic, radiometric, spectrographic, and chemical analyses of the products. Kline (20) has published a guide for examining placer areas; it includes methods used by the Bureau of Mines for making such evaluations.

Of the source minerals under consideration in this presentation, those containing columbium and tantalum are the least abundant. Known worldwide reserves of columbium-tantalum minerals are small. There probably always will be a delicate balance between the ore supply and the requirements for these critical and strategic metals. The United States at present depends almost entirely upon foreign sources for its supply of these raw materials. Known reserves of columbite in this country (in South Dakota, North Carolina, Arizona, and Colorado) have been estimated at 125,000 pounds; this estimate does not include the columbite content of the bauxites of Arkansas, the columbium-bearing titanium minerals also in Arkansas, or any reserves in the Idaho and Montana deposits. Tantalite reserves have been estimated at about 115,000 pounds and microlite (a calcium tantalate) at about 600,000 pounds. Until the placer deposits of the Pacific Northwest have been evaluated thoroughly, actual columbium-tantalum reserves cannot be accurately determined.

PRODUCTION

Idaho (<u>21</u>)

Electrically operated, converted bucketline gold dredges on Big Creek in Valley County have been producing black-sand concentrates containing monazite, ilmenite, zircon, and garnet. Only monazite has been marketed; the other minerals were accumulated as concentration rejects.

Baumhoff-Marshall, Inc., in January 1951 started operating a 6-foot Yuba dredge in the area. It had an 80-foot digging ladder with 80 buckets, each having a 6 cubic-foot capacity, and was capable of reaching a depth of 35 feet below the water level. Average capacity per 24-hour period was 5,000 cubic yards. Late in the summer of 1951 Idaho-Canadian Dredging Co. put into operation a Yuba dredge of the same size and capacity, but the digging ladder was 13 feet longer, there were 4 more buckets, and it could reach a depth of 45 feet. About the same time the Warren Dredging Corp. started operating a 4-foot boat in the same area. The company operated its dredge until May 1953 when an accident caused it to capsize. Salvage of the equipment has been completed, but it has not been put back into operation.

Separation procedures were similar on the 6-foot dredges. The buckets emptied into a 6- by 48-foot trommel screen having Yuba plates drilled with 3/15- and 1/4-inch round holes. Undersize flowed to double Pan American jigs arranged on each side of, and at right angles to, the trommel. With this arrangement recovery was increased, because all sand flowed across two cells. The resulting rougher concentrates were dewatered then cleaned by two jigs of the same type. A 400-cubic-foot storage tank located amidships held the finished product until it was pumped ashore.

Treatment of the concentrates before trucking to Cascade differed. The product from the Baumhoff-Marshall dredge was pumped directly to a 10-ton dump truck on the bank. Idaho-Canadian pumped from the dredge to a Symons V screen with 24-mesh screen cloth. Oversize (nearly all ilmenite) was discarded, and undersize went to a 3-foot dewatering cone. The thickened pulp was pumped to a 25-ton steel loading bin. Concentrates from both operations were trucked to Cascade and stored separately while awaiting shipment by rail to Boise.

At the concentration plant in Boise the sand was dried in a rotary kiln and passed over electrostatic and magnetic separators. The monazite was bagged and shipped to processors. An ilmenite-magnetite-garnet fraction and a zircon-quartz fraction were stored awaiting possible re-treatment into usable products if a market is provided.

Oregon (22)

The urgent need for chromium during the early part of World War II drew attention to the black-sand occurrences on the ancient marine terraces along the southwest coast of Oregon. After extensive exploration the Krome Corp. was organized to exploit the deposits in the Seven Devils district about 17 miles south of Marshfield. Mention of the operation is intended to illustrate another method for mining and milling beach sands. Although chromite was the primary product, substantial quantities of zircon were recovered and stockpiled.

The Krome Corp. originally planned to install a wet gravity concentrator near the mine, which would produce a low-grade bulk concentrate. This product was to be processed at a magnetic separation plant near the railroad at Beaver Hill. Carryalls and scrapers were to be used to remove the overburden, and mining was to be done with power shovels. The ore proved to be quite soft, and carryalls were used almost exclusively for the entire operation. A slackline with a 6-cubic-foot scraper was tried on several occasions.

The ore was treated by wet separation methods. Wet screens, rolls, and rod mills were used to disintegrate and scrub the material before desliming in a hydroseparator. Unclassified feed was put over large deck tables at a rate of about 6 tons per hour; the middlings were sized and retabled. The bulk concentrate from the tables was collected in a sump and pumped to a cone ahead of a 4-cell flotation unit, which functioned as a scrubber, to remove the last traces of adhering slime. In the final step the cleaned bulk product, containing about 35 percent Cr_2O_3 and a substantial quantity of zircon, was dewatered and belt-conveyed to a concrete storage platform to await trucking to the magnetic plant.

The Southwestern Engineering Co. built and operated the magnetic concentration plant at Beaver Hill for the Defense Plant Corp. Here the dried bulk concentrate was separated into various fractions by progressive stages of magnetic intensity. After passing through an indirect oil-fired drier the concentrate was put over a vibrating screen to remove any tramp material present and carried by a screw conveyor to 100-ton storage bins which fed 5 induced-roll-type magnetic separators. highly magnetic fraction containing magnetite, ilmenite, and high-iron garnet was removed by the first pass over the rolls. The tailings from this pass were distributed to 3 high-intensity separators to yield 4 chrome products and 2 offgrade products. Rejects from this operation were put over a special magnetic separator to produce another chrome product and tailing composed chiefly of zircon with smaller quantities of minerals with low magnetic susceptibility. This product was treated on a crossbelt separator, resulting in two chrome products and zircon-rich tailing. All of the chrome fractions were combined and transported to a surge bin ahead of the flotation department. After conditioning the garnet was removed in a six-cell flotation unit. The chrome product (tailing) was dewatered, dried, and stockpiled. The zircon-bearing fractions were put over tables to produce a high-grade product by removing silica. A small quantity of rutile remained. The zircon product was dewatered, dried, and sent to storage.

The plant closed on January 1, 1944, just 30 days after certain of the Government's domestic chrome purchase agreements had been suspended. Several modifications in plant operation, including installation of 64 Humphreys spirals to replace the shaking tables, had been completed shortly before the closing date.

Zircon from this operation was used by the Bureau of Mines at Albany, Oreg., in the original research which resulted in development of the magnesium-reduction

process (Kroll process) for producing ductile zirconium metal. Before the reduction research, the Bureau's mineral-dressing staff investigated methods for beneficiating the stockpiled product to acceptable grade. In addition to gravity-concentration and magnetic-separation techniques, selective froth-flotation procedures were studied. Although the product was amenable to froth flotation, in general, a high-grade concentrate with reasonable recovery was difficult to obtain. Results of earlier research by the Bureau of Mines on the Oregon sands have been published (18).

Upgrading of chromite concentrates stockpiled during World War II was begun in 1955 by Pacific Northwest Alloys, Inc., under a contract with GSA. Electrostatic and electromagnetic methods are being used to produce a clean chromite concentrate before shipment to the company plant near Spokane, Wash., where ferrochrome is produced. Completion of work on the stockpiled material is expected by the end of 1956.

In the same area, near Bandon in Coos County, the first recovery of chromite from the beach deposits since the above-mentioned World War II operations was in prospect in 1955. Plans to mine the chromite-bearing sands by open-pit methods and to utilize an acid leach to lower the iron content of the concentrates, thereby improving the chrome-iron ratio to a point acceptable to the Grants Pass Purchase Depot, were announced, and construction of facilities was begun.

TECHNOLOGY AND USES

Chromium

The uses of chromite are manifold; perhaps the best known application is the familiar use of chromium in plating various types of metalware to provide a durable and beautiful finish. Other common uses are in the making of refractories, stainless steels, various high-temperature alloys and high-strength structural steels, and in miscellaneous categories such as leather tanning, pigments, pyrotechnics, and photographic supplies. Chromite ores may be used directly in manufacturing refractories and in the chemical industry. Its use in the steel industry usually involves preliminary preparation of various types of ferrochromium, although in certain instances the ore is added directly to steel furnaces.

Titanium

Titanium usually is considered a light metal and not in the rare category, but because it probably is the most abundant constituent of the black sands it will be treated briefly. Like zircon, most of the ilmenite consumption is for nonmetallic purposes. The metal, however, is being produced in increasing quantities and is finding new applications. Titanium is light, strong, and corrosion resistant. In alloy form it is much stronger than aluminum alloys, and its tensile strength and hardness approach that of certain alloy steels. Its strength and lightness fit it for use in jet aircraft and lightweight armor plate, and its corrosion resistance, especially to salt water, opens many possibilities for marine applications.

Much has been published on ductile titanium in recent years; a general background may be obtained by referring to these articles (23 24 25 26 27 28).

Zirconium and Hafnium

Zirconium and hafnium can be considered together. The two metals are associated intimately in nature and, because of their similar chemical behavior, have presented separation problems. It became apparent during the early stages of the research directed toward using zirconium metal for nuclear reactors that for such

applications zirconium would have to be virtually free of hafnium. A suitable method was developed, and in 1951 the Bureau of Mines at Albany, Oreg., began producing zirconium and hafnium in quantity.

Hafnium is ductile and corrosion resistant but not as favorably as zirconium. Opposed to zirconium, it has a very high absorption cross section for thermal neutrons. Hafnium has potential use in radio tubes, incandescent lamps, and rectifiers and cathodes for X-ray tubes because of its high melting point and high degree of electron emission. Zirconium is used in the nuclear reactors powering the U. S. S. Nautilus, the world's first atomic-powered submarine. Potentially it can be used in applications requiring corrosion resistance, ductility, and strength. Hafnium's high-absorption cross section suggests use as radiation shielding material. The oxide and carbide, because of their extreme melting points, are of current interest in the development of superrefractories for jet engines, nuclear reactors, and other high-temperature devices.

Several comprehensive publications covering the production and properties of ductile zirconium are available. For details, the reader may care to consult these publications (29 30 31 32).

Rare-Earth Metals and Thorium

Johann Gadolin and A. G. Ekeberg in 1794 and 1797, respectively, thought that the metallic oxide they had separated from a recently discovered mineral was that of a single element. They did not dream that it was a mixture of about 15 elements. Ekeberg suggested the name yttria for the new oxide and gadolinite (in honor of the Finnish chemist) for the mineral.

In later years, the term "rare earths" was used to designate this group of elements which have similar chemical properties. The term was selected because of their relative scarcity at the time of naming and because their oxides resembled alkaline earth oxides, which were well known. Members of the group, arranged in order of decreasing abundance, are: Cerium, neodymium, lanthanum, samarium, gadolinium, dysprosium, ytterbium, erbium, praseodynium, lutecium, terbium, holmium, thulium, and europium.

The names of the elements of the rare-earth group have been derived from a variety of sources (33). Yttrium, erbium, terbium, and ytterbium are named after Ytterby, the Swedish village from which gadolinite was first obtained. Europium is a geographical name. Holmium was derived from Stockholm; lutecium from Lutetia, an ancient name for Paris; and thulium from Thule, an old name for Scandanavia. Samarium received its name from samarskite, in honor of a Russian mining engineer named Samarski, and cerium was named for the asteroid Ceres. Didymium means the twin element, so named because of its close resemblance to lanthanum, from which it was separated. When didymium was found to contain two elements, one was called neodidymium, the new twin, but the name was shortened to neodymium. Praseodymium signifies a green-color twin. Lanthanum is derived from the Greek verb meaning to lie hidden, and dysprosium means difficult of access.

The rare-earth elements are listed in the periodic table between atomic Nos. 57 and 71, inclusive (see table 4). Yttrium is not in this series of atomic numbers but is so similar to the rare earths chemically that it is usually included in the family. Thorium, atomic No. 90, also is similar in properties and, because it occurs in association with the rare earths, is often included with them. Promethium, No. 61, is unknown in nature and has been identified only as a fission product of uranium.

	Τ	Atomic	Atomic	
Element	Symbol	No.	weight	Discoverer and date
Cerium group				
Lanthanum	La	57	138.92	Mosander, 1839.
Cerium	Ce	58	140.13	Claproth, Berzelius, Hisinger, 1803
Praseodymium	Pr	59	140.92	von Welsbach, 1885.
Neodymium	Nd	60	144.27	Do.
Promethium	Pm	61	146.0	Marinsky and Glendenin, 1945 - separated from atomic pile at Oak Ridge.
Samarium	Sm	62	150.43	Boisbaudran, 1879.
Terbium group		[
Europium	Eu	63	152.0	Demarcay, 1901.
Gadolinium	Gd	64	156.9	Marignac, 1880.
Terbium	Тb	65	159.2	Mosander, 1843.
Dysprosium	Dy	66	162.46	Boisbaudran, 1886.
Yttrium group				
Holmium	Ho	67	164.94	Cleve, 1879.
Erbium	Er	68	167.2	Mosander, 1843.
Thulium	Tm	69	169.4	Cleve, 1879.
Ytterbium	Yb	70	173.04	Marignac, 1878.
Lutecium	Lu	71	174.99	Urbain, 1907.
Yttrium	Y	39	88.92	Gadolin, 1794.

TABLE 4. - Rare-earth elements

Thorium was discovered more than a century ago by the Swedish chemist Berzelius, who isolated the element from the mineral thorite. The element was named after Thor, the Norse god of war.

Cerium and lanthanum are the predominant rare earths in both monazite and bastnaesite. Approximate oxide analyses, in percent, for the 2 minerals are (1) monazite-cerium, 29; lanthanum, 16; praseodymium, 4; neodymium, 11; samarium, 1; and the remainder, less than 1; and (2) bastnaesite-cerium, 35; lanthanum, 25; praseodymium, 3; neodymium, 8; samarium, 1; and the remainder, less than 1. In addition, monazite contains thorium in quantities ranging from less than 1 to more than 10 percent.

Some of the rare earths appear as fission products when uranium and thorium are bombarded with neutrons. As a group, the rare earths are good absorbers of slow neutrons; gadolinium is the best absorber known.

Properties (34)

The chemical and physical properties of the rare-earth compounds characterize their similarity. The elements in this group usually are trivalent and form basic oxides and insoluble oxalates and fluorides in mineral acids. Addition of oxalic or hydrofluoric acid to mineral-acid solutions generally effects a separation of the group from other elements.

Because of the similarity in properties separation of the individual elements in the group has been difficult, but for many practical applications, this separation does not seem to be necessary. Recent developments, however, of separation and purification techniques have made many high-purity rare earth compounds available.

In general, the rare-earth metals have a silver-gray luster, are good heat conductors, and are fair conductors of electricity. Their hardness increases with the atomic number; those of the cerium group can be cut with a knife. The metals are malleable when free of oxygen, but oxide inclusions reduce this malleability.

Moist air tarnishes the metal rapidly, but the resulting oxide film spalls off, exposing more metal to oxidation. The rare-earth metals are soluble in dilute acids and react with hot and cold water. Concentrated sulfuric acid does not react readily with the metals. They are active reducing agents and are capable of reducing many metal oxides. Cerium will ignite in air between 150° and 180° C. The group combines directly with halogens above 200° C., with nitrogen above 1,000° C., and with almost all metals to form alloys.

The rare earths, except lanthanum and lutecium, are characterized by sharp absorption bands in the ultraviolet, visible, and near infrared regions of the spectrum, which result in the characteristic beautiful pastel colors of the rare-earth salts.

According to Spedding (35), cerium is soft, ductile, and iron-gray. It melts between 770° and 800° C. and, when heated in the form of wire, burns brilliantly. Its pyrophoric property makes it the active ingredient in lighter flints. It is the most easily purified member of the rare-earth group because it can form compounds other than oxides in which it has a valence higher than 3. Cerium metal is also a powerful reducing agent.

Lanthanum, in the pure metallic form, is soft, ductile, and has a melting point of about 870° C. It oxidizes in air and is attacked slowly by cold water and rapidly by hot water. Colorless salts result from its reaction with acids. The metal becomes superconducting at a few degrees Absolute. It has a very radioactive isotope, which may be produced in atomic piles. The oxide has found application in the optical industry because it yields a special noncorroding glass of high refractive index for cameras and other instruments.

Gadolinium, when chilled, has ferromagnetic properties similar to iron; however, it loses these strong magnetic properties when warmed to room temperature. Dysprosium reportedly is also ferromagnetic at low temperatures.

Thorium is a soft, heavy, gray metal that is difficult to fuse. It is stable at ordinary temperatures and is not affected by water, even at 100° C. It has a specific gravity of 11.75, fuses at 1,827° C., and boils above 3,500° C. When heated in air it burns brilliantly, forming the white oxide (ThO₂). Thorium is radioactive and subject to nuclear fission when bombarded with neutrons.

Mesothorium, the first radioactive disintegration product of thorium, ranks next to radium in importance. Like radium, its disintegration products emit the alpha, beta, and gamma rays characteristic of radioactive substances. Mesothorium decays at least 250 times faster than radium, and therefore, in its pure state, weight for weight, its radioactivity would exceed that of radium. Mesothorium may thus serve as a substitute for radium in luminous and therapeutic purposes. It can be used also for the more expensive radioactive tracers. Its high rate of gamma-ray emission more readily affects Geiger counters and consequently makes tracing its course much easier. Mesothorium is obtained as a byproduct in the manufacture of the thoria used in the gas-mantle industry. Its output is governed by the demand for thorium nitrate and cerium compounds.

Processing (36)

Sulfuric acid usually is employed to open monazite. In general, commercial practice consists of digesting a mixture of monazite and sulfuric acid in a castiron pot that is fitted with a vented cover so the acid fumes may be removed and recovered. Solubility of the thorium present depends upon the quantity of sulfuric acid used; equal weights of monazite and 98 percent acid plus fuming sulfuric acid will result in an insoluble thorium compound when the reacted mass is added to water. In this case, the insoluble thorium compound can be removed by filtration and the rare-earth metals recovered from the filtrate. An increased quantity of sulfuric acid and no fuming acid will yield thorium in a soluble form. It can be removed by precipitating with sodium pyrophosphate or a base.

Phosphoric acid formed during the digestion must be removed after separation of thorium from the solution. This can be accomplished by precipitating the rare earths with oxalic acid or sodium sulfate. The desired compound is recovered by filtration, and subsequent treatment depends upon the ultimate product required. The chloride, which is used in the preparation of misch metal (a mixture of all the rare earths in metal form), is made by dissolving the precipitate in hydrochloric acid and evaporating to dryness in an atmosphere of hydrogen chloride.

Commercially, cerium metal and misch metal are produced by the electrolysis of the fused chlorides in a melt containing calcium, sodium, or potassium chlorides. The container, an iron pot, is the cathode and an iron rod or carbon rod is the anode. The metal, which collects in the molten state is cast into plates. Alloys are made by adding the rare-earth metal to the alloying agent in the molten state under a cover of molten salts to prevent oxidation.

A direct high-temperature chlorination process that is under development has been described recently in the literature and offers an advantage over the acid-leach process (37). In this method unground monazite sand and powdered charcoal are briquetted by pressing or formed into granules in a rotating drum through which water-saturated air is passed. The briquets or granules are dried and screened. The chlorination reaction is carried out in an alundum tube furnace at about 900° to 1,000° C. Dry nitrogen is admitted during the heat-up period to expel air and moisture. Dry chlorine then is passed through the tube. The chlorination yields about 95 percent anhydrous chlorides; their chief impurities are magnesium and calcium chlorides. The advantages of this process include the elimination of phosphorus and the formation of rare-earth chlorides in a single operation. Impurities, such as iron, titanium, chromium, zirconium, tin, and silicon, as well as thorium, are eliminated as volatile chlorides, from which the thorium can be recovered later. The anhydrous rare-earth chlorides can be drained from the bottom of the furnace as a liquid.

Sometimes monazite is opened with sodium hydroxide instead of sulfuric acid. The alkaline process is more costly than the sulfuric acid methods; however, it makes possible the preparation of phosphate-free and thorium-free rare-earth compounds. This method usually is limited to high-grade monazite concentrates and to processing when the recovery of thorium is of secondary importance. Research workers at Battelle Memorial Institute, Columbus, Ohio, recently described a process for recovering thorium and rare earths from monazite concentrates. The following steps are involved in this process (38):

 Reaction of the monazite sand with a hot, concentrated aqueous solution of sodium hydroxide that converts the metal phosphates of the sand to hydrous metal oxides and trisodium phosphate.

- 2. Separation of the hydrous metal oxides from the dissolved sodium phosphate and excess sodium hydroxide.
- 3. Dissolution of the hydrous metal oxide in hydrochloric acid.
- 4. Precipitation of a thorium product by partial neutralization of the acid solution.
- 5. Subsequent precipitation of a high-grade rare-earth hydroxide product by further neutralization of the chloride solution.

Bastnaesite is treated differently (39). There are no appreciable thorium and no phosphate present to contaminate the final products. Sulfuric acid can be used to digest the bastnaesite; but, because of the fluorine present, it is necessary to equip the iron pots with fume-recovery systems to collect the hydrofluoric acid evolved. If bastnaesite is treated directly with dilute acids, the efficiency of the rare-earth recovery is not high, because insoluble rare-earth fluorides form that are difficult to handle and are contaminated with the gangue materials. After the bastnaesite is in solution, the rare-earth products can be made in the usual manner. Commercial preparations of rare-earth metals are made by electrolysis of the fused rare-earth chlorides. Calcium reduction of the anhydrous chlorides is used when very pure metals are desired. A mixture of the appropriate anhydrous chloride and ground calcium metal is placed in a tantalum crucible and heated in a bomb to between 650° and 750° C. A booster in the mixture initiates an exothermic reaction, which rises to about 1,400° C. This reaction results in a calcium rare-earth alloy, from which the calcium can be removed by volatilization in a highvacuum induction furnace. Spedding (40) has prepared high-purity rare-earth metals in small quantities for use as spectrographic standards.

The difficulty of separating the rare-earth elements has hindered their exploitation. The chemical similarity of the rare earths makes it an enormous task to separate them in pure form by chemical methods. Fractional crystallization and other chemical reactions that take advantage of slight differences in properties can be used, but the task is very time consuming. It has been reported that as many as 40,000 operations have been necessary to get some of the rare earths in pure form. Research since 1945 has shown that another method of separating the earths, a much more rapid method than fractional crystallization, has evolved in the form of an ion-exchange process. This method depends on the ionic properties of materials and is very effective for separating closely related substances that cannot be isolated easily by ordinary chemical reactions. Much of this ion-exchange work was done by Frank H. Spedding and his associates at the Ames Laboratory of the AEC, Iowa State College (35). A number of commercial firms are producing the rare earths by either chemical or ion-exchange methods. This latter method is not used commercially for separating the cerium group, because fractional crystallization is more economical. The latest developments at Iowa State College were reported by Spedding and Powell in a recent paper (41). Research on the ion-exchange method also was conducted at the University of Illinois under contract with the Office of Naval Research (42).

Recently, a solvent-extraction separation using counter-current-extraction techniques has been developed (43). This appears to be a practical separation method based on fractionation of an aqueous solution of mixed rare-earth nitrates by selective extraction with immiscible tri-n-butyl orthophosphate. The extraction coefficients of the rare earths are approximately equal throughout the entire series.

It has been pointed out above that thorium is separated from the rare earths in the early part of the monazite processing. The thorium is converted to oxalate, digested with sodium hydroxide, and then dissolved in hydrochloric acid. This solution is treated with sodium hydroxide, precipitating thorium hydroxide that can be purified in three ways: (1) Oxalate method, (2) carbonate method, and (3) sulfate method. The final product after purification is thorium nitrate Th(NO3)4·4H2O]. According to a British patent, a mixture of thorium oxide and calcium (98-100 percent excess over the theoretical amount required to reduce ThO2) is heated by high-frequency induction in a molybdenum crucible, first in a vacuum up to 700° C. and then in an inert gas at 1,400° C. for 10 minutes (44). After cooling, the reaction mixture is leached thoroughly with dilute acetic acid to remove the calcium and calcium oxide, and the resultant thorium powder is dried in a vacuum. The powder is pressed into pellets that can be melted in vacuum in a beryllium oxide pot or sintered in vacuum at 1,200° to 1,400° C. and then cold-worked.

Industry

The following firms are the principal processors of monazite:

Domestic

Lindsay Chemical Co., West Chicago, Ill. Maywood Chemical Works, Maywood, N. J. Rare Earths, Inc., Pompton Plains, N. J

Foreign

Thorium, Ltd., London, England.
Societe de Produits Chimiques des Terres Rares, Paris, France.
Treibacher Chemische Werke, Treibach, Austria.
Oriquima do Brazil, Sao Paulo, Brazil.
Indian Rare Earths, Ltd., Alwaye, Travancore, India.

In addition to the monazite processors, the following produce high-purity compounds:

M and L Rare Earths Co., Murray, Utah. Research Chemicals, Inc., Burbank, Calif. Research Laboratories of Colorado, Inc., Newtown, Ohio. Michigan Chemical Co., St. Louis, Mich.

The following firms are producers of misch metal and ferrocerium:

Domestic

Cerium Metals Corp., New York, N. Y
New Process Metals Corp., Newark, N. J. (subsidiary of Ronson Lighter Co.)
General Cerium Corp., Edgewater, N. J.
American Metallurgical Products Co., Pittsburgh, Pa. (Lan-cer-amp)
Mallinckrodt Chemical Works, St. Louis, Mo.

Foreign

Shawinigan Chemicals, Ltd., Shawinigan Falls, Quebec, Canada. Belgo-Canadian Mfg. Co., Ltd., Montreal, Canada.

Imperial Chemical Industries, Ltd., Liverpool, England. Sibor Hard Metals, Ltd., London, England. Chemo Metals, Ltd., London, England. British Flint & Cerium Mfg., Ltd., Tonbridge, Trent, England. Société de Produits Chimiques des Terres Rares, Paris, France. Treibacher Chemische Werke, Treibach, Austria. Promethus, Kempten, Germany. Société Anonyme de Pont-Brule, Brussels, Belgium. Monacerium, Ltd., Lisbon, Portugal.

The Molybdenum Corporation of America is beneficiating and processing bastnaesite at Mountain Pass, Calif.

Uses

As early as 1885, monazite was processed to make thorium nitrate for use in incandescent gas mantles, and the rare earths were a byproduct; but, as a market developed for the rare earths, thorium was relegated to byproduct status. Thorium mantles, which contain about 99 percent thoria and 1 percent ceria, still are used widely abroad, and, in this country. Modern application is in the well-known Aladdin kerosine lamps and the Coleman gasoline lantern. The armed forces used millions of these mantles during World War II.

Because of the difficulty experienced in separating the rare-earth group into its individual members, most established commercial applications utilize the natural combination in metal, alloy, or compound form. Misch metal, the mixture of all of the rare-earth elements in metallic form, contains 94 to 99 percent of rare metals, distributed as follows: 50 percent cerium, 18 percent neodymium, 5 percent praseodymium, 1 percent samarium, and 24-26 percent lanthanum, and others. Calcium, carbon, aluminum, silicon, and iron are the main impurities. Because of the predominant constituent, the product often is referred to as cerium. The pyrophoric property of ferrocerium, an alloy of iron and misch metal, makes the material desirable for the flints used in mechanical lighters. This property has made tracer bullets and luminescent shells possible. The ferrocerium alloy contains 18 to 30 percent iron.

Metallic thorium is used in the filaments of tungsten lamps and vacuum tubes, as a getter, and in X-ray tube targets. When mixed with tungsten and molybdenum, thorium forms a ductile alloy capable of being drawn into fine wires required in electronic discharge elements; the luminosity is increased, and the filaments are less brittle as a result of the thorium addition. An alloy containing 0.005 to 10 percent thorium is suitable for the electrodes of neon lamps. A mixture of thorium carbide and iron carbide has been used for electrodes in ultraviolet-ray-producing sun and health lamps.

When thorium-232, the naturally occurring isotope, is bombarded by neutrons, it is converted into fissionable uranium-233 in a quantity that may exceed the original quantity of uranium-233, uranium-235, or plutonium-239 consumed in supplying the stream of neutrons required for the conversion. This operation of creating an excess of nuclear fuel is known as breeding. This fact makes thorium an outstanding source of energy. The AEC has conducted research on a breeder pile at the National Reactor Testing Station, Arco, Idaho.

Large quantities of rare-earth fluorides and oxides are used as cores for high-luminosity carbon electrodes. Ordinary carbon arc lamps, although of high intensity, dissipate much of this intensity in the infrared region of the spectrum.

Addition of the rare-earth compounds results in a brilliant white light because of the intensification in the visible region. High-speed photography has been made possible by the use of these high luminosity electrodes (45).

Other uses of the rare earths as a group in compound form are mainly for glass and metal polishing, waterproofing, mildewproofing, weighting and dyeing of fabrics, glass manufacturing, and compounding of printing inks and phosphors.

The use of separated rare earths in compound form is increasing steadily. The oxidizing effects of cerium compounds has led to their use in photography, as oxidizing catalysts in organic preparations, and as ingredients in driers. Uses of the various cerium compounds are listed below:

Cerium oxide

- In the manufacture of special container glass to prevent passage of ultraviolet light which causes certain foods to deteriorate, as an opacifier in porcelain coatings, as an abrasive for polishing lenses and mirros, and in the manufacture of photosensitive glass and glass for windows in radiation shields (prevents darkening of glass by radiation).

Cerium hydrate

- As an ingredient in optical glass and in coloring and decolorizing glass.

Ceric-ammonium-

nitrate

- As a scavenger in production of explosives.

Cerium nitrate

- In the manufacture of Welsbach gas mantles, for tanning leather, in the ceramic and textile industry, and as an antiseptic.

Cerium oxalate

- Treatment of nervous disorders and as a sea-sickness preventitive.

Ceric sulfate and cericammonium-

sulfate - In volumetric analysis.

Lanthanum oxide has found application in the optical industry because it yields a special noncorroding, silica-free glass of high refractive index for aerial photographic lenses and other optical instruments. Lanthanum-ammonium-nitrate is used for atomic energy applications. Cerium and lanthanum are in commercial use as driers and catalysts for paints and protective coatings. Cerium and lanthanum naphthenates and octolates offer the following attributes to producers of heat-reactive coatings: Increased cross linking, tougher and hotter films, wide scope of activity at normal baking temperatures and cycles, and excellent color retention. Additions of these compounds effect cost savings by lowering the amino-resin requirement, improve water and soap resistance of films, and give better efficiency in baked films than is obtained with other metallic driers. Threatened shortages of critical drier materials, such as cobalt, during the Korean War drove researchers to survey the roster of undeveloped but promising drier metals.

Neodymium salts, characterized by a blue-red color, are used to make colored glassware. The salts also are used to decolorize glass containing iron oxide. Neodymium oxalate is used in the fabrication of high-temperature crucibles.

Praseodymium salts are used in the ceramic industry for coloring glass and glazes.

Neodymium and praseodymium have very strong absorption bands in the yellow region of the spectrum. A mixture of these in oxide form is used in manufacturing special glass for glassblowers' and welders' goggles. Better-grade sunglass lenses containing this mixture provide a sharp cut off of ultraviolet light. A neodymium-praseodymium mixture classically has been referred to as didymium, but now the term is used commercially to denote a cerium-free mixture of the entire group. Didymium carbonate is used in certain radio condensers.

Gadolinium oxide is used for atomic energy applications. Europium and samarium salts are used as activators in red and infrared phosphors.

No uses have been developed for compounds of the other members of the rareearth group.

Thorium oxide has a melting point of 2,800° C., and its use in high-temperature refractories takes advantage of this property. Thoria also is used as a petroleum-cracking catalyst and as a catalyst in oxidizing ammonia to nitric acid, carbon monoxide to water gas, and sulfur dioxide to sulfur trioxide. High-purity thoria is used as a constituent in special optical glass and in certain dental powders and pastes. Thorium salts have astringent and tonic properties and have been used to combat certain parasitic skin infections.

In addition to the uses mentioned above, there are several additional potentially important metallurgical applications of the rare earths. The addition of rare earths (misch metal) to magnesium produces cast alloys having elevated-temperature properties markedly superior to those obtainable with the older alloys. With suitable treatment, creep strengths of 8,000 p.s.i. at 200° C. can be developed in the new alloys, compared with 1,500 p.s.i. for the magnesium-aluminum-zinc type. Creep strength is one of the major factors in selecting material for elevated-temperature applications. Loads are applied to castings used in jet engines, for example, that persist for several hundred hours during which the engine is expected to give satisfactory service. Over this period, the material gradually deforms until proper functioning of the engine is impossible. Use of this alloy makes possible a significant decrease in deadweight and increased load capacity, speed, and range of operation.

The Cerium Metals Corp. published a summary of achievements made in application of misch metal alloyed with aluminum and magnesium up to September 1945 ($\underline{46}$). Subsequently, Marande ($\underline{47}$), Leontis ($\underline{48}$), and McDonald ($\underline{49}$ $\underline{50}$) of the Dow Chemical Co. reported further progress.

Leontis (51) showed that additions of thorium in quantities up to 3 percent significantly increase the ductility and the strength of rolled magnesium sheet. Thorium also contributes strength and creep resistance to magnesium at elevated temperatures in both the cast and wrought states. A magnesium-thorium-cerium alloy also was studied. The cerium was added as high-purity metal and not as commercial misch metal. Results of the experiment indicated that additions of thorium increase the strength of magnesium in the sand-cast state at room and elevated temperatures but decrease the ductility as measured by the elongation in the tension test. Only mild grain-refining action results from the addition of thorium. These alloys exhibit remarkable temperature resistance, as illustrated by the relatively small loss in strength between room temperature and 300° C. The magnesium-thorium alloys are similar to magnesium - rare-earth (misch metal) alloys in this behavior. The level of strength properties in magnesium-thorium alloys, however, is lower than that observed in magnesium alloys containing rare-earth metals such as didymium (cerium-free misch metal) and misch metal of equivalent alloy content. Magnesium-thorium

alloys exhibit high resistance to creep at elevated temperatures. The creep resistance of magnesium-thorium alloys at 260° and 310° C. is the highest observed to date in any magnesium alloy.

Addition of 3 percent cerium to alloys containing 3.6 and 10 percent thorium increases the yield strength of these alloys at temperatures up to 205° C. but has no effect on the tensile strength. The increase in yield strength is accompanied by a marked decrease in elongation. Comparison with the properties of magnesium plus 3 percent cerium alloy shows that all the magnesium-thorium-cerium alloys have higher strength properties; however, the magnesium-thorium-cerium alloys still are not equivalent to the best magnesium-rare-earth alloys.

American Metallurgical Products Co., Pittsburgh, Pa., is marketing a product known as Lan-cer-amp (52). This product contains more lanthanum than regular misch metal and is being made for ladle additions in stainless, tool-steel, alloy, and electrical steel grades. Additions are made in the amounts of 3/4 to 6 pounds per ton of steel. Variations in the ratio of the individual rare-earth elements, particularly lanthanum v. cerium, apparently influence effectiveness, in that highlanthanum misch metal gave more pronounced benefits in steel than ordinary grades of misch metal. Because of the inherent difficulties of separation, economic reasons dictate that rare earths necessarily be added to steel as a group. However, it is possible, by proper selection of ores and smelting techniques, to obtain a product that will impart the desired benefits efficiently. Results of using Lan-cer-amp treated steel castings show higher impact strength and ductility in a quenched and tempered condition than do untreated heats. Increased fluidity of treated metal is characteristic, and a 20° C. drop in the solid-liquids temperature has been noted. Less grain coarsening in austenitic stainless steels, type 310, is experienced when 2 pounds of Lan-cer-amp per ton is used.

Rare earths (misch metal) added to cast iron act as powerful oxidizers and aid in removing of slag from the molten metal. Resistance to scaling at higher temperatures and resistance to certain corrosive atmospheres also result. Additions to malleable iron melts act as a carbide stabilizer.

Several of the research staff of Carpenter Steel Co., Reading, Pa., have been investigating variables that affect hot workability of stainless steels for some time (53). As a result of their work, they determined that rare-earth elements are effective in promoting and improving the hot workability of austenitic chromiumnickel and high-alloyed stainless steels when added as alloying elements.

A paper presented at the Electric Furnace Steel Conference, Iron and Steel Division, AIME, in Pittsburgh, December 4-6, 1952, pointed out that considerable information has been reported by American and British authors regarding the use of cerium in the production of nodular cast iron and by Carpenter Steel Co. listing the advantages of using rare-earth elements in stainless steels (54). However, little information has been reported regarding the effects of rare-earth elements on common cast steels. The experiences American Steel Foundries had with these elements when added to steel seem to indicate that improvements were noted in ductility, impact strength, inclusions, hot tears, fluidity, sulfur reduction, porosity, weldability, and feedability.

The addition of rare earths (misch metal) to hot-dip aluminum baths gives smooth coatings on mild-steel parts without the use of a flux (55). Misch metal added to pure aluminum baths increases and thickens the amount of oxide on the bath; however, the increased thickness of the oxide surface does not increase coating difficulties. Instead, the iron-aluminum compound that causes lumps to

appear on the coated surface without the misch metal addition is dispersed and distributed uniformly throughout the coating.

The beneficial effects of rare earths in certain heat-treated aluminum alloys have been known for some time. An aluminum alloy containing 1.5 percent manganese and 4.5 percent misch metal can be forged more easily than Dural, and an aluminum alloy with 11 percent misch metal has stress-rupture properties superior to present commercial alloys in the range of 370° to 425° C. (56).

Tests show improved microstructure of castings from secondary aluminum when alloyed with cerium. Cerium-aluminum alloys may be heat-treated to obtain improved tensile strength, elongation, and hardness. These alloys are recommended for piston applications where creep and fatigue are important considerations because of elevated service temperatures.

The rare-earth metals are superior to aluminum and silicon and equal to magnesium as deoxidizing agents for copper and copper alloys. Small additions of rare earths to a copper alloy containing nickel and silicon reportedly make them heat hardenable.

Nickel alloys are made more resistant to oxidation by additions of the rareearth metals (57). Appreciable grain refinement has been observed in alloys containing nickel and copper, and the castability of the alloys is improved.

To summarize, the rare earths (misch metal) improve the tensile properties of cast iron, improve the hot-workability of austenitic chromium-nickel and other high-alloyed steels, and, when added to hot-dip aluminum baths, make it possible to obtain a smooth coating on mild-steel parts without the use of a flux. The rare earths can be alloyed with aluminum, magnesium, copper, nickel, and zinc. The creep resistance of extruded magnesium is improved by such additions.

Columbium and Tantalum

Columbium and tantalum are in demand because of their exceptional and unique properties for certain purposes compared to other metals. Moreover, the known worldwide resources of the ores of these two materials are exceedingly small; and, in view of the great need that the United States would have for these metals in an emergency, the Government is exerting every effort to encourage exploration and development of mineral reserves wherever present.

The most extensive use of columbium is in alloys with steel, where it is an excellent stabilizer, maintaining an austenitic condition of steel at room temperature. Such steel alloys have all the desirable characteristics of solid solutions and are extremely ductile while maintaining good strength at high temperatures. Columbium is lighter in weight than iron, is more readily fusible, and is softer even than tantalum. It is malleable and can be welded at red heat. Columbium can be worked easily into wire and sheet and has excellent corrosion-resistant properties, though not quite so good as tantalum. The metal will not tarnish in air at room temperature, but at high temperatures it becomes coated with an oxide that prevents further oxidation. Pure columbium is insoluble in sulfuric, hydrochloric, and nitric acids and in aqua regia but will dissolve slowly in hydrofluoric acid. It is not attacked by alkali solutions, although it can be fused by solid alkalis and carbonates to form columbates.

The valuable properties of columbium in imparting stabilizing characteristics to steels are extended still further by the high-temperature suitability of its

alloys as used in jet engines and gas turbines. Columbium alloys are now in direct competition with other stainless steels for these purposes. The metal decreases the tendency of steel to air-harden and increases the toughness, weldability, ductility, and corrosion resistance of chromium steels. In steel castings that require welding without subsequent heat treating, the harmful effect of carbide precipitation may be eliminated by adding columbium to the steel. The carbon alloys itself with the columbium instead of the chromium, thus stabilizing the chromium alloy by forcing the crystal boundaries to retain their chromium content. Hence, intergranular corrosion does not occur. The creep strength and impact strength of alloys are increased by the addition of columbium. Ferrocolumbium contains 40 to 50 percent columbium, and ferrocolumbium-tantalum contains about 60 percent combined columbium and tantalum. A chromium-nickel-columbium steel has strength properties adequate for applications in rotor forgings and in blades and tubes used in gas turbines. Columbium is an excellent getter in vacuum tubes at high temperatures because it absorbes gases better than tantalum and most other metals. It therefore has extensive uses in the electronic industries. Columbium also can be employed as a rectifier and as a cathode material in the electrolytic determination of copper, zinc, silver, and nickel.

Tantalum also has excellent chemical resistance to most corrosive materials. It is affected by hot sulfuric acid and by hydrofluoric acid but is inert to all other inorganic acids and salts. It has extensive application in the chemical industry where corrosion-proof containers are needed for processing chemicals and producing new products and is used extensively by dentists and surgeons for interior repairs to the human anatomy. It has a high mechanical strength and can be welded easily to other tantalum-metal parts. It forms an alloy with iron, making ferrotantalum, which has great strength and creep resistance. It also combines with tungsten to provide an elastic alloy used for filament springs and hooks in electronic tubes. In toolmaking, tantalum carbide is used extensively as a cutting edge; it is used also on the edges of such tools as bulldozer blades and on the bucket of draglines, cranes, and shovels. Tantalum at certain temperatures becomes superconductive and can be used for a liquid-level gage for liquid air, liquid helium, and other liquid gases. Tantalum-potassium fluoride is a catalyst in the manufacture of synthetic rubber and is used extensively for that purpose. It forms a good anode and a grid material for tubes of various types, particularly those that must withstand high temperatures and high voltage. The metal has a high melting point and a low vapor pressure. Tantalum's melting point is almost 3,000° C., which is higher than almost any other metal, and yet the pure metal is as soft as copper in its pure state. It can be hardened easily by heat treatment or cold working; the metal also is hardened if it contains dissolved gases or impurities. Its low linear coefficient of expansion enables it to be sealed into glass and permits its use for crucibles. The electrical resistance of tantalum is greater than that of tungsten and almost 10 times as great as copper. It is a white, lustrous metal and is tough and malleable. All of these properties make tantalum valuable in many ways, and in emergencies, such as an intensified preparedness program or war, it is almost indispensable for these exceptionally important uses. The metal can be drawn into wire for use as a filament in incandescent lamps but has been largely superseded by tungsten for this latter use. Tantalum is used in rectifiers and can eliminate B-batteries in radio sets for this reason. The trickle charger was developed using tantalum as the rectifying metal. Tantalum can be machined with regular steel cutting tools by using carbon tetrachloride as a cutting compound and can be welded to several other metals by electric processes, although arc welding is difficult and torch welding impossible. Although it is relatively inactive to most reagents at temperatures approaching 200° C., its reactivity increases greatly, allowing it to combine chemically with many materials, such as chlorine, fluorine, and bromine, as well as most of the inorganic acids.

Recovery of tantalum and columbium from tantalum ores by means of fused-salt electrolysis is being practiced by the Fansteel Metallurgical Corp., North Chicago, Ill., for years the principal producer of columbium and tantalum in the United States. The tantalum in separated from columbium by preparing the potassium double-salt with the metal. Pulverized ore is converted to tantalocolumbic acid by fusion with caustic soda and treatment with hydrochloric acid. The tantalocolumbic acid then is dissolved in hydrofluoric acid, and enough potassium salt is added to form tantalum-potassium fluoride and columbium-potassium fluoride. The solution of these compounds is allowed to cool, and the tantalum salt, which is less soluble than that of columbium, cyrstallizes out, leaving the columbium in solution. A filtration step completes separation of the two metals.

In subsequent steps, the potassium double salt with the metal (for example, potassium-tantalum fluoride) is electrolyzed, and the tantalum produced is found in the form of powdered metal in the electrolyte. The electrolyte is dissolved in water, washed thoroughly, and then tabled so that the purified metal can be collected in the form of a powder. It then can be treated by powder-metallurgy methods or melted to an ingot, cast, and rolled. Small quantities of impurities influence the properties of both tantalum and columbium; but, in general, starting with tantalite or columbite and using the fused-salt electrolysis methods, it is possible to obtain a fairly pure product.

As is indicated above, columbium also is obtained by fused salt electrolysis of the double salt, potassium-columbium fluoride, and must be treated either by powder-metallurgy methods or by melting to ingot form the powder obtained during the electrolytic process. The process as now used is somewhat expensive because the potassium-tantalum fluoride is rather expensive to prepare, the hydrofluoric acid alone amounting to something over \$1 per pound.

Columbite ores are processed by the Electro Metallurgical Division, Union Carbide & Carbon Corp., Niagara Falls, N. Y. This company produces ferrocolumbium and ferrotantalum-columbium. Columbite-tantalite ores are processed by Kennametal, Inc., Latrobe, Pa., to make columbium-tantalum-bearing carbides.

Another source of columbium-tantalum-containing material has been the slags resulting from smelting tin ores, principally from Belgian Congo. The Bureau of Mines, Albany, Oreg., as well as other research groups, has studied the problem of separating columbium and tantalum from these slags by liquid-liquid extraction. Preliminary results of the research have been favorable. It has been possible to obtain substantially pure tantalum from columbium and vice versa by using various organic solvents and complexing agents.

PRODUCTION, IMPORTS, AND CONSUMPTION

Chromite

Domestic production of chrome ores increased from 404 short tons in 1950 to 152,418 tons in 1955 as a result of the establishment of a Government stockpiling program in 1951. Imports of chromite varied from a low of about 1,304,000 short tons to a high of about 2,227,000 tons over the same period, and consumption averaged about 1,125,000 short tons.

Ilmenite

Since 1950 annual domestic ilmenite production has averaged about 530,000 tons and consumption approximately 697,000 tons. During the same period imports of ilmenite have averaged 170,000 tons.

Zircon

Domestic zircon production has been substantial, yet figures are company confidential and cannot be released for publication. Since 1950 consumption of zircon has averaged about 31,000 tons and imports 22,000 tons.

Rare Earths and Thorium

Production of monazite in the United States began in the Carolinas in 1893, and from 1895 to 1910 this country and Brazil supplied the world's needs. A small but thriving domestic industry was established, but the total output was only about one-tenth that of Brazil. United States production was negligible for most of the period 1910-48, while annual imports for the same period averaged more than 1,000 tons. Thorium salts, mostly nitrates, and gas-mantle scrap were imported in addition to the monazite. During much of this same period mantles were imported as well as exported by this country.

Misch metal was also an item of trade, and during 1924-53 imports of this product ranged from less than 100 pounds annually to 33,000 pounds in 1945 and averaged about 5,000 pounds. Imports of rare-earth compounds were at a maximum in 1951, reaching 822,125 pounds. From 1942-53 United States exports of misch metal and similar alloys ranged from a low of 26,000 pounds in 1942 to a high of 182,000 pounds in 1947. Table 5 shows domestic and world production of monazite from 1893 through 1947; data from 1948 are classified and cannot be published. Imports of rare-earth compounds and misch metal, and exports of ferrocerium are listed in table 6.

Consumption statistics for the rare-earth metals and thorium metal are classified.

Nonenergy consumption of thorium compounds for 1950-54 has averaged about 32,700 pounds of contained thorium dioxide (58). According to this report, during the same period, consumption by categories was gas-mantle manufacture, 24,700 pounds; refractories and polishing compounds, 1,300 pounds; chemical and medical, 5,700 pounds; and electrical, 1,000 pounds. In addition, during 1953 and 1954, 3,600 pounds and 4,600 pounds, respectively, were used in magnesium alloys.

Columbium and Tantalum

Domestic production of the ores of these metals is measured in pounds. The average output for 1950 and 1951, measured as mine shipments, was about 1,000 pounds. As the result of recovery of columbite as a byproduct of the spodumene operations at Kings Mountain, N. C., shipments increased in 1952 to slightly over 5,000 pounds. Shipments in 1954 totaled almost 33,000 pounds. Imports of columbium ores between 1941-54 varied from about 1.4 million pounds in 1941 to a high of 6.8 million pounds in 1954. Tantalum-ore imports were a minimum of 127,600 pounds in 1948 and a maximum of 982,000 pounds in 1954. Most of the columbite came from Nigeria and the bulk of the tantalite from Belgian Congo. Combined consumption in 1954 was estimated to be about 200 tons of contained metal.

TABLE 5. - Monazite

TABLE 5 Monazite					
Production, short tons			Imports		
Year	United States	World total	Year	Short tons	
1893	65	65	1909	35	
1894	273	273	1910	227	
1895	787	4,094	1911	353	
1896	1.5	207	1912	278	
1897	22	271	1913	409	
1898	125	2,274	1914	385	
1899	175	3,107	1915	937	
1900	454	2,087	1916	1,218	
1901	374	2,185	1917	2,914	
1902	401	1,729	1918	1,497	
1903	431	4,067	1919	316	
1904	372	5,729	1920	907	
1905	672	5,563	1921	-	
1906	423	5,220	1922	1,733	
1907	274	5,165	1923	127	
1908	211	5,684	1924	273	
1909	271	7,392	1925	-	
1910	50	6,043	1926	335	
1911	-	4,996	1927	597	
1912	_	5,018	1928	442	
1913	-	2,967	1929	577	
1914	- 10	1,989	1930	1 609	
1915	18	1,743	1931	1,698	
1916	19	1,467	1932	1,569 56	
1917	11	3,436	1933 1934	112	
1918	_	2,944 2,428	1934	1,299	
1919	_	3,189	1936	607	
1920 1921	_	1,861	1937	336	
1921	1 -	379	1938	456	
1923		276	1939	1,560	
1924	_	725	1940	2,965	
1925	1	196	1941	3,448	
1926		293	1942	4,398	
1927	_	693	1943	4,980	
1928	_	340	1944	384	
1929	_	386	1945	816	
1930	_	33	1946	2,726	
1931	-	100	1947	2,013	
1932	-	1,063	1948-present	(1)	
1933	-	605		ŀ	
1934	_	1,128			
1935	-	4,278		į	
1936 1937	1 -	3,678 4,325			
1938	-	6,639			
1939	-	5,027			
1940	- 2	4,913			
1941 1942	2	4,578 3,163			
1942	-	3,845			
1944	-	2,261			
1945	-	2,891			
1946 1947	_	1,445 1,921			
1947	(1)	(1)			
1/ 5 1	1	1161-1	····		

1/ Production and import figures classified.

TABLE 6. - Processed monazite, in pounds

	Imports	Exports	
Year	Rare-earth compounds	Misch metal	Ferrocerium
1923	44,799	-	-
1924	122,489	100	(1)
1925	22,093	89	(1)
1926	11,627	1	(1)
1927	86,858	71	(1)
1928	100,826	2,085	(1)
1929	133,985	2,524	(1)
1930	88,120	861	(1)
1931	397	-	(1)
1932	(1)	-	(1)
1933	(1)	44	(1)
1934	(1)	_	(1)
1935	(1)	-	(1)
1936	(1)	22	(1)
1937	(1)	-	(1)
1938	(1)	-	(1)
1939	(1)	-	(1)
1940	(1)	462	(1)
1941	(1)	20,191	(1)
1942	(1)	11,573	26,016
1943	119	5,720	54 , 797
1944	106	20,240	38,918
1945	-	33,080	32,175
1946	-	15,660	39,718
1947	-	665	182,204
1948	-	1,600	55,133
1949	4,436	220	70,009
1950	177,161	1,000	55,273
1951	822,125	699	85 , 849
1952	135,515	4,921	37,121
1953	(1)	4,211	94,913

1/ Data not available.

OUTLOOK

Interest has been focused upon the alluvial sands of the Pacific Northwest since 1950, primarily because of the monazite content of the Idaho deposits. This mineral, required for national defense, was in very short supply in this country because of restricted imports from India and Brazil, our main sources, since 1946. Extensive field-exploration programs indicated quantities of monazite that could be made available for industrial and stockpiling purposes, provided the financial incentive was great enough. The demand dictated the price, and dredging operations for this strategic mineral were begun early in 1951. It was apparent from the beginning that, after the initial requirements had been satisfied or after imports were resumed, in order to compete with other sources, the incentive for continuing production of Idaho monazite would have to be provided by the Government in the form of a subsidy or a local market would have to be established for the other heavy-mineral constituents. In 1952 shipments of monazite concentrate from South Africa began to reach our industry, and by the middle of 1955 the Idaho dredging operations ceased because of a weakened market.

Further activity in Idaho based solely on the rare-earth content of the monazite probably is not too likely. Expansion of our rare-earth-processing industry over the potential of imports - or during periods of interrupted shipments - will not revitalize dredging operations in Idaho necessarily, because any increased demand for rare-earth raw materials can be met by production of bastnaesite from California and New Mexico deposits. The possibility of increasing requirements for thorium, not present to a significant extent in bastnaesite, as a source of nuclear energy could encourage renewed interest in Idaho monazite. Producers of monazite concentrate have been paid on the basis of the rare-earth content, with little or no value assigned to the thorium. In future the value of thorium may be greater than that of the rare earths, and higher prices may be paid accordingly.

The outlook for the other heavy-mineral constituents must be considered to evaluate the potentiality of the Northwest deposits.

Prospects for chromite from the Oregon beach placers are not promising after withdrawal of the Government stockpile program (to be concluded June 30, 1959, or when 200,000 long tons has been received at the Grants Pass Ore-Purchase Depot, whichever occurs sooner) or other Government-sponsored programs. Chromite from this source must necessarily compete with higher grade, lower price foreign imports, except during periods of Government support, as at present.

Expansion of titanium-metal production in this country must be geared to the use of ilmenite or high-titania slags because sufficient quantities of rutile, the desired raw material, are not available domestically. Concentrates of ilmenite from deposits in the Pacific Northwest must be consumed relatively close to the source owing to the high freight structure, which precludes successful competition in distant markets (this applies to the other constituents as well).

It is reasonable to expect that the demand for ductile zirconium will increase as the use of nuclear reactors continues to expand. Zirconium remains the most satisfactory structural metal readily available for this application. Use of the metal in other than the nuclear energy field probably will develop as soon as enough metal is available. Any increase in the output of zirconium for use in reactors will result in a more plentiful supply of hafnium. Research on the properties and possible uses of this metal will continue. Byproduct zircon could be recovered at present as part of the chromite operation in Coos County, Oreg.

The dependence of the United States upon foreign supplies of columbium-tantalum minerals seems to offer consolation as far as continued development and exploitation of domestic alluvial deposits are concerned. This, however, is not the "open sesame" at the present time. Metallurgically, the columbium-tantalum-bearing minerals (radioactive blacks) found in these deposits are refractory. They are complex multiple oxides of columbium and tantalum containing, in addition, titanium, thorium, uranium, and several rare earths. Their processing is much more difficult than that of uncomplicated columbite or tantalite, mainly because of the presence of titanium. Research in this direction is progressing satisfactorily, and it is hoped that many of the problems will be solved in the not too distant future. The Bureau of Mines staff at Albany, Oreg., has published results of beneficiation studies on samples containing radioactive blacks from deposits in Valley and Elmore Counties, Idaho (59). Research is being conducted by the same group on the extraction and separation of the columbium, tantalum, uranium, and rare earths (together with thorium) found in these minerals. Publications covering the separation of columbium and tantalum by liquid-liquid extraction have been prepared (60 61 62).

Mention should be made of the potentiality of magnetite and garnet found associated with the other heavy minerals. Magnetite is present in rather substantial quantities in many of the deposits. It cannot be considered important enough to support a steel industry in the Pacific Northwest; but, should such an industry be developed, the magnetite from these sands probably could contribute significantly to the operation. A small quantity of the garnet recovered at the Boise concentration plant has been sold to the roofing industry for use as granules. Individual grains of the garnet have some desirable abrasive qualities; and, although the competition is very keen, some outlet for that purpose might be developed.

In this report an attempt has been made to establish the existence of alluvial deposits in the Pacific Northwest containing a special assemblage of minerals in quantities sufficient to support a considerable industry. Utilization of these minerals seems dependent upon location of the processing plants within the general area. As we progress into the atomic age, more and more interest is being shown in the rare metals; research and development programs directed toward the production and application of these metals are increasing steadily. As a result, there will be an urgent need for an expanded processing industry. The availability of low-cost hydropower, a wide selection of plant sites, and the other desirable features found in the Pacific Northwest make this area potentially important. The trend toward industrialization along the Pacific coast points up the outlook for markets and heightens the possibility of establishing a processing industry based upon these alluvial deposits.

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