

Information Circular No. 10

IDAHO BUREAU OF MINES AND GEOLOGY

MOSCOW, IDAHO

JUNE, 1961

Metals from Blacksands

SELECTED TECHNOLOGIC AND ECONOMIC DATA

State of Idaho

ROBERT E. SMYLIE, Governor

Idaho Bureau of Mines and Geology

E. F. COOK, Director

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by

C. N. Savage

IDAHO BUREAU OF MINES AND GEOLOGY
Moscow, Idaho



Figure 1. Blacksand separation plant designed to recover columbite, euxenite and monazite; ilmenite, magnetite, zircon, and garnet are by-products. Operated by Porter Bros. Corporation at Lowman, Idaho. Treatment of dredge concentrates at this mill includes: electromagnetic, high tension electrostatic, and gravity separation. Capacity of the mill is 150 to 200 tons per day; recovery is 88.44 percent.

FOREWORD

For those readers of the Bureau's Bulletin 17, **ECONOMIC GEOLOGY OF CENTRAL IDAHO BLACKSANDS**, who may not be abreast of the rapidly changing technology and new uses of the metals contained in Idaho blacksand deposits, this Information Circular has been prepared by the same author as a companion publication.

E. F. COOK
Director
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TABLE OF CONTENTS

	Page
ABSTRACT.....	1
INTRODUCTION	1
NATURE OF AND NEED FOR THE ELUSIVE METALS	2
CURRENT TRENDS IN METALLURGICAL INVESTIGATIONS.....	3
TECHNOLOGY AND ECONOMICS OF SELECTED MINERALS AND METALS.....	5
Zirconium and hafnium	5
Titanium.....	12
Niobium (columbium) and tantalum	16
Thorium, scandium, yttrium, and the lanthanide (rare earth) metals.....	20
OUTLOOK.....	30
REFERENCES CITED	32

TABLES

Table 1a. Basic data pertaining to elusive elements	6
Table 1b. Basic data pertaining to familiar elements.....	8
Table 2a. Zirconium and hafnium prices.....	9
Table 2b. Zirconium prices.....	10
Table 3a. Ilmenite prices: concentrate and slag	13
Table 3b. Titanium prices.....	14
Table 3c. Titanium metal production and consumption.....	14
Table 3d. Titanium production in Idaho.....	14
Table 4. Niobium-tantalum domestic production	18
Table 5. Lanthanide or rare earth series	21
Table 6. Composition of didymium.....	22
Table 7a. Prices of thorium products	23
Table 7b. Prices of thorium nitrate, oxide, and chloride	24
Table 8a. Prices of rare earths.....	26
Table 8b. Prices of rare earth oxides.....	27
Table 8c. Prices of cerium and lanthanum oxides.....	27

ILLUSTRATION

Blacksand separation plant designed to recover columbite-euxenite and monazite; ilmenite, magnetite, zircon, and garnet are by-products Frontispiece

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ABSTRACT

The exact amount of blacksand minerals contained in Idaho placers is not definitely known, but their quantity and potential value are known to be fairly high. The elusive metals in certain of these placer minerals have unusual physical, structural, and nuclear properties that make them versatile. They are light and strong, tough and durable, and resist corrosion, corrosion, high temperatures, and radiation damage. Such characteristics are needed by metals in the rapidly advancing space-age.

Among the more promising metals in Idaho's detrital blacksands are zirconium, hafnium, titanium, niobium (columbium), tantalum, thorium, scandium, yttrium, and the lanthanides (rare earths).

Research and development, now proceeding rapidly in blacksand geology and metallurgy, will determine the proportions of any future exploitation. New uses are being developed for some of these metals, while unit prices are being reduced.

The outlook for thorium, scandium, yttrium, and the rare earths is uncertain at present; however, zirconium and hafnium, titanium, and niobium and tantalum should develop moderately expanding markets.

INTRODUCTION

Because blacksand deposits of known or potential value in Idaho are relatively plentiful, the Idaho Bureau of Mines and Geology published in the fall of 1957 an information circular briefly summarizing blacksand characteristics, possible uses, and economic significance (Prater, 1957). Just before this publication, because of the growing interest in Idaho placer mineral deposits, Bureau personnel had been assigned to several projects involving field, laboratory, and library investigations of blacksands.

In 1960 and early 1961, the Idaho Bureau of Mines and Geology released two additional publications on Idaho blacksands. The first described placer deposits of the Elk City region (Reid, 1960), while the second was a comprehensive study of the nature, origin, and occurrence of blacksands in central Idaho (Savage, 1961).

In the 1957 publication, Prater (p. 12-13) accurately summarized the status of Idaho's placers; his statements are still applicable:

Any discussion at this time of the economic future of blacksands in placer deposits is largely speculation. To date their commercial exploitation has been based upon some strong demand for one particular mineral. . . . The industry would be on a much firmer foundation and operations could be expected to be on a more continuous basis if markets could be developed for several of the minerals. . . . It would seem, however, that the full utilization of the minerals composing the bulk of the blacksands is contingent upon the development of industries that consume these minerals in this area. . . . The total tonnage of blacksand minerals available in Idaho placer deposits is not known but certainly it is considerable.

The following discussion will emphasize the nature and uses of metals which may be derived from blacksand minerals, some technology of their extraction, and selected economic factors pertaining to the use and future of these commodities.

NATURE OF AND NEED FOR THE ELUSIVE METALS

Metals from blacksand minerals have been variously referred to as: "miracle metals," "rare earths," "rare metals," "newer metals," "future metals," "highly reactive metals," "elusive metals," and "less familiar metals." A majority of these terms describe correctly within limits, but most of them cannot be applied to all the metals in the group: many of the "rare metals" are not "rare earths"; though titanium metal is not "common," titanium is certainly not a "rare element"; and although titanium and zirconium are "highly reactive," they resist corrosion as well as stainless steel does and because all these blacksand metals are difficult to produce in the pure metallic state, the term "elusive metals" is appropriate (Tables 1a and 1b).

We are becoming more familiar with these elusive metal substances every day, but whether or not they are "miracle metals", providing answers for all kinds of industrial problems remains to be proved.

The urgent need for materials of unusual physical, structural, and nuclear properties is indicated by intimations in occasional releases of classified information about industrial and governmental research projects that developments in basic research are being slowed down by lack of suitable structural materials. For example, the metallurgical industry will have to catch up with the planning and drafting stages of new propulsion motors and new equipment designed for space travel.

Contemporary designers need versatile structural materials--suitable metals and alloys of improved quality to meet the demands of the future. Metals are needed that are light and strong, tough and durable, and that will resist high temperatures and radiation damage. Also needed are metals which have special magnetic, non-magnetic, and electrical properties.

CURRENT TRENDS IN METALLURGICAL INVESTIGATIONS

In the search for space-age metals important new metallurgical data are being collected daily by industry supported studies at Battelle Memorial Institute, at Stanford Research Institute, and at many state, federal, and company-owned laboratories. Outstanding in this work is the progress in powder metallurgy and in the development of new uses for "old" metals. Production of ferroalloys has made surprising advances since the first electro-smelting work in 1892 at Spray, North Carolina. Now, more than 50 major alloys of chromium, silicon, vanadium, tungsten, zirconium, columbium-tantalum, boron, calcium, and titanium are being produced for the insatiable appetite of the steel industry alone.

Combinations of ceramic materials and metals are being used to produce carbides, nitrides, borides, and silicides--substances with high chemical stability, resistance to oxidation, high strength, and low density. Such progress is opening a whole new field of ceramic-metals called cermets. These major strides in the development of metallurgical and structural materials are only a prelude to the development that must take place in more advanced stages of an era of atomic power and space travel.

Space research has produced a number of new uses for several metals long known but in little demand. Sherwood (1958, p. 1455-1459) of Battelle Institute noted that some of the metals could now be classified by the manner in which they react with oxygen at high temperatures. Among the metals he cited are zirconium, hafnium, molybdenum, niobium, tantalum, rhenium, and chromium. For those interested in further investigation of the subject, Sherwood included an extensive list of references in his publication. This list indicates the trend in research toward a future use and demand for little-known minerals; the magnitude of this demand is unpredictable.

Blocher and Campbell (1958, p. 9) experimented with niobium, tantalum, and zirconium carbides in an attempt to produce structural materials useful at very high temperature. Some of their findings indicated that the coatings were good: none of them cracked or spalled when cooled to room temperature or when reheated to a temperature of 2,000° C. Such experiments will undoubtedly continue because resistance to stress under high temperatures is one of the major problems of modern space-age metallurgy.

Now under investigation are such applications of these new metals as oxidation- and corrosion-resistant zirconium alloys; welded zirconium tubing; niobium

and tantalum alloys for aircraft, space craft, electronics and chemical engineering industries; alloys of niobium and numerous other metals for high ductility; corrosion resistant tantalum alloys; and other various applications too numerous to mention.

Niobium (columbium), having a low thermal-neutron cross section, is one of the great potential bases of alloys for structural materials. One of its applications is in the development of atomic reactors for energy and propulsion. Commenting on the metal niobium, Sims (1958, p. 342) emphasized some of its properties:

Columbium (niobium) has very interesting mechanical properties. Although its room temperature strength is moderate, strength is retained with very little decrease as temperature increases...the ultimate tensile strength of columbium at 1200° F is approximately the same as at 200° F....

Zirconium-uranium alloys are also receiving attention from metallurgists. Research on the corrosion behavior of these alloys as affected by water temperature, uranium content, and oxygen content, is a particularly promising phase of the work. Meanwhile, Berry and Peoples (1958, p. 414t) indicate that the low absorption cross section of zirconium for thermal neutrons suggests possible use of the product Zircaloy to clad alloys which contain up to 60 weight percent uranium. According to their report, a Zircaloy envelope will probably resist corrosion and prevent contamination of the cooling water stream by fission products. Certainly this rate of progress will influence the production, use, cost, and the future of the elusive minerals and their metals. Referring to them as the "future metals," Ogden (1958) states that there is little doubt of a promising future for such heavy metals as tungsten, tantalum, molybdenum, and niobium; and particularly that their greatest potential use is for urgently needed structural materials with high strength at high temperature.

Gonser (1958, p. 14) concludes there has been

...the feeling that in these uncommon metal elements lies a greater opportunity for interesting and valuable discoveries by research than in the more prosaic work of improving older metals and their alloys...the supply situation is practically no problem.

Among other trends, Gonser points out that the future appears good for the semi-conductors among the newer metals; that important uses also are being found for some metals that have poor structural qualities; and that uses are even being found for metals with high melting points. Combinations of these elusive metals with "old" (familiar) metals, often yield interesting and valuable results.

Further, Gonser emphasizes the potential of elusive metals in the chemical industry. With the production of reactive metals and pure metals by chemical metallurgy, the chemical industry is fast becoming a prime producer of space-age metals.

Table 1a, which lists the percentages of the less common, elusive, metallic elements in the earth's crust, indicates some of the minerals whose physical characteristics are of growing importance to the metallurgist and structural engineer. Note the high melting points of both niobium and tantalum and the high melting points of zirconium and yttrium oxides.

For comparative purposes Table 1b includes the more familiar metallic elements showing the same type of data used in Table 1a.

TECHNOLOGY AND ECONOMICS OF SELECTED MINERALS AND METALS

Zirconium and hafnium

As early as 1921 the U. S. Bureau of Mines published a bulletin (Marden and Rich, (1921) dealing with investigations and possible uses of zirconium metal, its oxides, and related products. Noting the widespread occurrence of zircon in placer deposits, this exhaustive report (p. 6) stated "...recently as much as 3 percent of some of the auriferous sand of Idaho has been found to be zircon mixed with some monazite." But not until 35 years later were extensive bibliographies of zirconium studies prepared for the U. S. Bureau of Mines (Abshire, 1957, 1958).

The chemical properties of zirconium and hafnium are similar except for fundamental differences in atomic weight, density, atomic number, and neutron cross section. Because the two metals are nearly inseparable, their separation was a major hurdle to early development of the pure metals. However, the slight difference in solubilities of certain mineral salts of the two elements made it possible to separate them commercially. Hafnium-free zirconium is called "reactor-grade" metal. Where the two metals are together in a mineral, hafnium occurs in smaller quantities than zirconium.

Five or six years ago, many of the less familiar metals--like zircon and hafnium--were unknown in a state of high purity. The few that had been so purified were expensive laboratory curiosities. Now several of these less common elements are produced in quantity and have important industrial applications. With purities from 99.8 to 99.997 now available, metallurgists can observe for the first time the true physical characteristics and important reactions of these metals. In some instances prices still remain prohibitively high; however, as technological problems are solved and as demand increases, a broad base of uses should develop and then prices will drop accordingly.

Table 1a

Basic data pertaining to elusive elements*

<u>Metallic element</u> (Symbol & mineral sources)	<u>Content in earth's crust</u> (Weight percent grams per ton)	<u>Melting point</u> (° C)	<u>Density</u> (Grams per c.c. atmospheric temp.)
Zirconium, Zr Zircon, baddeleyite	0.0220-199.54	1857 (Zr oxide, 3315)	6.44
Titanium, Ti ilmenite, rutile, sphene, anatase, leucoxene, brookite	0.44-3,991	1800 (Alloys, 649)	4.5 (18° C)
Niobium, Nb (Columbium, Cb) tantalite, columbite, pyrochlore, euxenite, samarskite, betafite, eschynite, fergusonite, formanite, hjelmite, polycrase, priorite	0.0024-21.77	2500 (Alloys, 1093)	8.4 (15° C)
Tantalum, Ta minerals same as for niobium	0.0002-1.9	2996 (Alloys, 2850)	16.6
Thorium, Th monazite, uranothorite, thorite, and others	0.0012-10.88	1750 (Th oxide, 3200)	11.72
Hafnium, Hf with zirconium in zircon	0.0005-4.08	2200	--
Scandium, Sc thortveitite and others	0.0005-4.53	1546-1596	3.02
Yttrium, Yt monazite, euxenite, bastnaesite, brannerite, fergusonite, samarskite, polycrase, priorite, xenotime, and others	0.0028-25.4	1546 (Yt oxide, 2410)	4.47

*Compiled from several sources listed in references cited.

<u>Metallic element</u> (Symbol & mineral sources)	<u>Content in earth's</u> <u>crust</u> (Weight percent grams per ton)	<u>Melting</u> <u>point</u> (° C)	<u>Density</u> (Grams per c.c. atmospheric temp.)
Lanthanum, La monazite, bastnaesite, fergusonite, samarskite, polycrase, priorite, xenotime, euxenite, brannerite, and others	0.0018-16.36	920 (La oxide, 2315)	6.16
Cerium**	0.0046-41.72	840 (oxide 2600)	6.77
Praseodymium, Pr**	0.0006-4.99	935	6.77
Neodymium, Nd**	0.0024-21.76	1024	6.77
Samarium, Sm**	0.0007-5.9	1052 (oxide 2350)	7.54
Europium, Ev**	0.0001-1.0	900 (oxide 2050)	5.17
Gadolinium, Gd**	0.000.6-5.8	1350 (oxide, 2350)	7.87
Terbium, Tb**	9×10^{-5} -0.8	1400- 1500	8.25
Dysprosium, Dy**	0.0005-4.08	1475- 1500 (oxide 2340)	8.56
Holmium, Ho**	0.0001-1.09	1475- 1525	8.80
Erbium, Er**	0.0003-2.27	1475- 1525	9.06
Thulium, Tm**	2×10^{-5} -0.2	1500- 1550	9.32
Ytterbium, Yb**	0.0003-2.54	824	6.96
Lutecium, Lu**	8×10^{-5} -0.7	1650- 1750	9.85

** Occurs in same minerals listed for lanthanum.

Table 1b

Basic data pertaining to familiar elements

<u>Metallic element</u> (Symbol)	<u>Content in earth's</u> <u>crust</u> (Weight percent grams per ton)	<u>Melting</u> <u>point</u> (° C)	<u>Density</u> (Grams per c.c. atmospheric temp.)
Oxygen (non-metal)	O	46.60-422,662	-218 1.14 (-184° C)
Silicon (semi-metal)	Si	27.72-251,257	1420 2.4 (20° C)
Aluminum	Al	8.13-73,739	1800 2.7 (20° C)
Iron	Fe	5.00-45,350	1535 7.85
Calcium	Ca	3.63-32,652	810 1.54
Sodium	Na	2.83-23,796	98 0.97 (20° C)
Potassium	K	2.59-23,582	62 0.87 (20° C)
Magnesium	Mg	2.09-18,956	651 1.74
Chromium	Cr	0.020-181.4	1615 6.63
Vanadium	V	0.015-136.05	1710 5.69
Zinc	Zn	0.013-117.9	420 7.04
Nickel	Ni	0.008-72.6	1455 8.75
Copper	Cu	0.007-63.5	1083 8.60
Tungsten	W	0.007-62.58	3370 18.85
Tin	Sn	0.004-36.3	232 7.29
Lead	Pb	0.002-14.5	327 11.34 (20° C)
Molybdenum	Mo	0.002-13.6	2620 9.01
Uranium	U	0.0004-3.6	1132 18.06- 19.04
Gold	Au	5 x 10 ⁻⁷ -0.0045	1063 19.3
Platinum	Pt	5 x 10 ⁻⁷ -0.0045	1773 20.37 (20° C)

Recovery of zirconium metal is rather complex. The first procedure involves further gravity concentration of the naturally concentrated zircon from blacksand placers. Pure zirconium metal is produced by converting the impure metal to the purified tetrachloride ($ZrCl_4$) and then reducing it to a metallic zirconium with magnesium (Kroll process). Some companies use sodium as a reducing agent instead of magnesium. The reagents must be very pure and the atmosphere in the reactor must be virtually free of oxygen, nitrogen, water vapor, or other active gases; even small traces of these substances will "alloy" with the metal and render it brittle.

The chloride produced from natural minerals is a mixture of $ZrCl_4$; when this is reduced to metal, it forms "commercial grade" zirconium, actually an alloy of zirconium and hafnium. Because "reactor-grade" zirconium must be hafnium-free, the salts of the two metals are separated by a solvent extraction process. Coffey (1958, p. 111) discusses this liquid-liquid extraction method stating:

The difficult hafnium-zirconium separation in the production of reactor-grade zirconium... uses ammonium thiocyanate in methyl isobutyl ketone to separate zirconium from the 2% hafnium.

The products from the liquid-liquid separation are reconverted to the tetrachlorides; when those are reduced by magnesium, they form reactor-grade zirconium and pure hafnium.

The van Arkel (iodide) process yields the highest grade zirconium, but it is essentially a refining process that requires a feed of crude zirconium metal.

Zirconium prices follow a pattern corresponding to that for the other "rare" metals: prices originally are high, then fall with improvement of metallurgical techniques and greater use. In 1927 zirconium metal (98 percent grade) was quoted at \$15 per pound (Ellsworth, 1932, p. 19). The following prices were quoted by the U. S. Bureau of Mines in 1956 (U. S. Bureau of Mines, 1956, p. 1008-1009):

Table 2a

Zirconium and hafnium prices

Zirconium metal powder, per pound.....	\$7.00
Zirconium ferrosilicon:	
12-15 percent Zr per pound	\$0.08 - 0.1075
35-40 percent Zr per pound.....	\$0.2525 - 0.3025
Hafnium metal powder (99.3 percent):	
per <u>gram</u>	\$25.00
Hafnium oxide (99.5 percent): per <u>gram</u>	\$17.00

Note that for the last two items prices are quoted for a gram; at this rate hafnium metal powder would sell at over \$11,350 per pound and hafnium oxide would sell at over \$7,720 per pound.

Kauffman (1957) quotes the following prices:

Table 2b

Zirconium prices

1943	Zirconium (iodide)	\$630 per pound
1945	Zirconium (iodide)	\$315 per pound
1953-56	Zirconium sponge averaged:	\$12 to \$15 per pound
1957	Reactor-grade zirconium sponge averaged:	\$4.75 to \$14.00 per pound

At the start of 1959 low-hafnium zirconium sponge, powder, and platelets were quoted (Eng. Mining Jour., 1959, p. 4) at \$7-14 per pound. In its most recent contracts, AEC purchased zirconium at an adjusted, weighted-average price of \$6.25 per pound (U. S. Bureau of Mines, 1960a, p. 1000-1001). Zirconium mill shapes are negotiated at ranges varying from \$11.00 to \$30.00 per pound. Domestic prices for zircon have averaged \$47.25 a short ton, f.o.b. mines.

The United States has been importing zirconium sponge (20-30 thousand ton per year) from Australia, Brazil, and Japan. Domestic consumption was about 65,000 to 75,000 tons in 1956 (Kauffman, 1957). In December, 1958, Engineering and Mining Journal's "Metal and Mineral Markets Reports," stated (p. 11): "Production and imports of zircon both declined about 55% in 1958... About 150 tons of reactor-grade sponge was imported from Japan." The same source stated that the U. S. exported 2,100 tons of zircon in 1958, principally to Canada. Wessell (1959, p. 1) indicated that domestic zircon production was about 30,000 tons in 1958 and that imports were 19,275 and 48,000 tons for 1958 and 1959, respectively.

In 1956, the U. S. Atomic Energy Commission announced a 2.2 million pound stock of reactor-grade zirconium would be required each year for a five-year-period. These requirements, and others, presumably are being filled by such established producers as the Wah Chang Corp., Albany, Oregon; the Carborundum Metals Co., Inc., Parkersburg, W. Va.; the Columbia National Metals Corp., Pensacola, Florida; and the Mallory-Sharon Metals Corp., Ashtabula, Ohio.

Zirconia is produced by the Titanium Alloy Mfg. Division, National Lead Co., and the Norton Co., Niagara Falls, New York; Lava Crucible Refractories Co., and Westinghouse Electric Corp. in the Pittsburgh area; Zirconium Corp. of America, Solon, Ohio; and the Norton Co., Huntsville, Alabama.

Zirconium is now available in the following forms: ductile metal of high purity, including reactor-grade metal; metal of varying zirconium content in sponge, ingot, or briquet form; metal powder, plate, sheet, bar, and strip form; wire; ferro- and nickel-alloy; and soluble salts.

The desirable properties of zircon from the industrial standpoint are workability, corrosion resistance, low neutron absorption, good thermal conductivity, chemical inertness, and affinity for oxygen (a "getter"). Hafnium has similar qualities except that it strongly absorbs neutrons in an atomic reactor (the principal reason for removing hafnium from reactor-grade zirconium metal).

Hafnium is available as sponge and metal powder; and in many compounds, such as oxides, borides, fluorides, chlorides, sulfates, nitrates.

Formerly, when the primary uses for zircon were restricted, little was known of the important properties of pure zirconium metal. By 1957, Kauffman indicated that the following percentages (of the total volume of zircon being consumed) were being used in industry:

- Foundry sand, 50 percent
- Refractories, 25 percent
- Metal production, 16 percent
- Ceramics and others, 9 percent

By 1958, according to several trade journals, the major uses were as follows:

In the metals industry, chiefly as structural materials:

1. Reactor-grade zirconium, pure metal;
2. Medical use, for body replacement parts in surgery;
3. Assorted alloys for resistance furnaces, linings for engines using high temperature propellants, and as alloys where toughness, strength and corrosive resistance are needed (including use in cold rolled steel).

In the chemical industry, chiefly as soluble salts (except where metals are employed in equipment):

1. Pigments and rubber;
2. Fabric industry as a mordant (dyes), and as a water repellent;
3. Medical use in the form of phosphates and carbonates.

In the ceramics industry:

1. Refractories requiring a very high melting point, e.g. stabilized oxides and borides of zirconium can withstand temperatures up to 2500-3300 degrees Centigrade;
2. Ceramics as an electrical insulator.

According to a recent report (Eng. Mining Jour., 1958, p. 11) most of the zirconium metal used in 1958 went into the construction of nuclear reactors. For example, reactors using zirconium metal are operating at Shippingport, Pa., Dresden, Ill., and Arco, Idaho. Zirconium metal also has been used in the construction of nuclear-powered merchant and naval vessels. Wessell (1959, p. 1-2) states that "...military requirements increased, principally for use in...units of a nuclear-powered navy.... Demand for hafnium remained high."

The supply of hafnium is small, but since it is a by-product of reactor-grade zirconium production, hafnium supplies should increase. At present, most of the hafnium consumed goes into carbide for cutting tools, into the production of fluorescent powders, and some into control rods for nuclear reactors.

Zirconium, relatively plentiful in the earth's crust and also occurring as it does in placers along with other economically important heavy minerals, should enjoy a good future. Its use in super-refractories and cermets is promising. Continued future use of zirconium in atomic energy reactors seems assured. Use of zircon sand in foundries may increase in the future.

Use of zirconium as an alloy for structural materials should expand in the future because the metal has many desirable characteristics, including good workability. The number of companies processing and fabricating zirconium metal is increasing. Competition between zirconium and hafnium and other metals like titanium, tantalum, and niobium is also increasing.

Titanium

Titanium, more abundant in the earth's crust than zirconium (Table 1a), is a common constituent of igneous rocks and an impurity in many iron ores. When iron ore contains high percentages of titanium, however, the iron is useless to industry. Titanium is frequently associated mineralogically with magnetite, niobium, and tantalum. The high titanium content in Idaho black sand deposits occurs chiefly in the mineral ilmenite. The titanium minerals rutile, sphene, and anatase also are present sparsely in these sands.

The U. S. Bureau of Mines published an exhaustive report on titanium (Miller, 1957). This handbook covers such diverse subjects as consumption, properties, and uses; mineralogy and geology; resources; prospecting, mining, and ore beneficiation; processing; structure of the industry; supply and distributions; marketing prices, etc. A long bibliography is appended. The U. S. Geological Survey also has published an extensive bibliography on titanium (Lawthers and Mark, 1957).

Many of the properties of titanium are similar to those of zirconium. Discovered by Gregor in 1790, the element was first used as an alloy as early as 1906, and its oxide was used as a pigment in paints by 1918. By 1948, titanium's combination of strength at relatively high temperatures (titanium-base alloys melt at about

600° C), lightness and relatively high resistance to corrosion brought the metal into a prominent position among structural materials.

Ilmenite (FeTiO_3) and rutile (TiO_2) are the principal ore minerals of titanium. These minerals are concentrated first by gravity and electrostatic methods. Slag produced from hematite-ilmenite ore also has become an important source of titanium.

Treatment or processing in the past has been by one of three different methods: (1) the Kroll process involving magnesium reduction, (2) a sodium reduction process, and (3) an electrolytic process (using crude metal or scrap).

Ilmenite may be smelted in an electric furnace producing a titanium-rich slag that contains approximately 75 percent titanium dioxide. This slag can be used to produce pigment-grade titanium dioxide or titanium chloride. Although the titanium chloride generally is the starting point for commercial metal production, the development of a direct chlorination method is a promising future method of production.

Titanium ore is obtained from several sources. About 7,000 tons per year come from Florida beach sands, a source of titanium-bearing rutile in the United States. Approximately 50 percent of our ilmenite, containing titanium, comes from National Lead's McIntyre mine at Tahawus, New York, and about 38 percent is produced by DuPont from the Florida beach sands mentioned above. The balance of U. S. ilmenite production is from Virginia and Idaho blacksands. Oaxaca, Mexico, and Australia supply some American rutile imports.

The cost of ilmenite is about 9 cents per pound; rutile is approximately 6 cents per pound, but its known reserves are far smaller than those of ilmenite. Miller (1957, p. 1) quotes the following prices (as of 1955):

Table 3a

Ilmenite prices: concentrate and slag

Ilmenite concentrate:

59.5 percent TiO_2 \$18-\$20 per short ton.
(Idaho's placer ilmenite is 45 percent TiO_2)

Rutile concentrate:

94 percent TiO_2 \$200 per short ton.

Titanium slag:

70 percent TiO_2 \$36 per short ton.

The following average prices for titanium products as of 1958 were reported by the U. S. Bureau of Mines (1960, p. 897):

Table 3b

Titanium prices	<u>per pound</u>
Titanium sponge, grade A-1.....	\$1.82
Titanium sponge, grade A-2.....	1.70
Sheet.....	10.10
Strip.....	9.25
Plate.....	7.37
Wire.....	7.25
Forging billets.....	5.02
Hot rolled bars.....	5.75

The U. S. Bureau of Mines quoted the following U. S. production figures for the titanium industry (short tons) for 1957 through 1958 (1960a, p. 893):

Table 3c

Titanium metal, production and consumption (short tons)	1956	1957	1958
	Sponge production.....	14,595	17,249
Sponge consumption.....	10,936	8,221	4,147
Scrap consumption.....	2,033	1,743	1,336
Ingot production (includes alloying constituents).....	11,688	10,009	5,408
Ingot consumption.....	10,860	10,428	4,971
Mill product production.....	5,166	5,658	2,594

Total consumption of ilmenite in all products for 1957-58 was 840,719 and 731,420 short tons (gross weight), respectively.

The following figures for titanium production in Idaho were compiled by the U. S. Bureau of Mines (Minerals Yearbooks 1954-58):

Table 3d

Titanium production in Idaho (short tons)		
1953 - 1,585	1955 - 1,330	1957 - 28,397
1954 - (not revealed)	1956 - 48,619	1958 - 2,223

Though not all the figures for annual value of titanium production in Idaho have been released, the estimated and actual values suggest that production value for the period of 1953-58 was close to \$490,000. Ilmenite sales for 1959 are known to have been slightly higher than for 1958, although the totals have not been revealed. The Idaho titanium shipped during this period was ilmenite, and was used chiefly for roofing granules, paint pigment, and aggregate in making heavy cement slurry for cementing oil wells.

The six titanium producing smelters operating in the U. S. in 1958 were:

Harvey, Aluminum Inc., Torrance, California
Mallory-Sharon Metals Corp., Niles, Ohio
Rem-Cru Titanium, Inc., Midland, Pennsylvania
Republic Steel Corp., Massillon-Canton, Ohio
Oregon Metallurgical Corp., Albany, Oregon
Titanium Metals Corp. of America, Henderson, Nevada

In 1957, titanium consumption for paint pigment dropped about 7 percent and consumption for welding rod coatings fell off about 6 percent. Stocks of ilmenite, rutile, and titanium increased 23 percent, 120 percent, and 61 percent respectively (Stamper, 1958, p. 6). By 1959, domestic consumption of ilmenite in the pigment field had reached a new high of about 918,000 short tons (U. S. Bur. Mines MMS 3078, p. 5).

The U. S. Bureau of Mines implemented a new research program for 1958-59 which emphasized investigation and appraisal of the U. S. titanium minerals, mining, and metallurgical industries. Bureau laboratories conducted studies to improve electrochemical and chlorination processes in titanium production. Laboratory scale experiments have already produced commercial-grade titanium tetrachloride from which a rutile-like substance with 93 percent TiO_2 can be produced. Idaho ilmenite was used (Barr, Gilbert, and Harper, 1959). These processes give promise that the U. S. may become less dependent upon foreign rutile. The market for Idaho ilmenite might expand if, among other things, an inexpensive method of upgrading could be developed to supplement new processing methods. As a co-product among other placer minerals, ilmenite could become economically important in the future.

Methods developed to produce a specific metal may be used to produce other metals. For example, should low temperature chlorination processes work for both niobium- and titanium-bearing minerals, similarly new alloys might become feasible as a result of production of several different metals by one method (Stamper, 1958, supplement, p. 2).

Many titanium products may now be obtained from ilmenite, rutile or titanium slag that has been processed to produce titanium dioxide or titanium tetrachloride. Titanium products produced from these latter two compounds include

powder, carbide, fused crystal, ceramics, welding-rod coatings, chemicals, fiber glass, titanium sponge, water-proofing agents, and organic chemicals. Titanium pigments are used in paints, varnishes, plastics, flooring, fabrics, rubber, paper, inks, and cosmetics.

Metallurgical products using titanium include alloys of aluminum, steel, and other metals. The use of titanium as a structural metal is still increasing rapidly; its chief use has been in the construction of aircraft for both military and private use. Its density--only 57 percent that of steel--explains its use in aircraft; however, titanium is used as a structural material only where temperatures do not exceed approximately 700° C. The transportation industry (surface vehicles) may use more titanium in the future. The use of titanium in ordnance, in marine applications, and in chemical equipment should increase.

Future demand for titanium is difficult to predict; but, as a substitute metal which is light and corrosion resistant under moderately high temperatures, it should enjoy a good future. There still are technological problems to be solved; but with lower production costs, titanium metal might become highly competitive with steel for many uses. However, Jaffee (1958) predicts that the use of titanium in military aircraft will decline. He believes the titanium metal industry will reach its maturity by 1975 and will level off at a production of 400,000 tons per year.

Niobium (columbium) and tantalum

Niobium and tantalum, which almost invariably occur together in the same minerals, have similar physical and chemical properties. Fortunately, their affinity for each other is not as strong as that of zirconium and hafnium. Titanium nearly always occurs with niobium and tantalum. As indicated in Table 1a, niobium is 10 times as plentiful as tantalum in the earth's crust and occurs in greater quantities than lead and molybdenum. Tantalum occurs in quantities equal to about one-half the amount of uranium in the earth's crust. Niobium and tantalum are characteristically associated with coarse-grained granitic rock, including acid pegmatites. These minerals concentrate into economically valuable deposits chiefly through accumulation in heavy detrital mineral placer deposits like those in Idaho.

The minerals tantalite, columbite, pyrochlore, euxenite, samarskite, betafite, eschynite, fergusonite, formanite, hjelmite, polycrase, and priorite, all contain niobium and tantalum. They also yield varying amounts of titanium, uranium, and the rare earth minerals.

Niobium and tantalum are extracted from placers by preliminary gravity concentration followed by more complicated processing. Niobium-tantalum concentrates are converted into an iron complex by carbon-arc reduction when ferroalloys are desired. Because this product does not require separation of niobium from tantalum, the operation is comparatively simple. When pure metals are desired, more intricate chemical processing is necessary. Fansteel Metallurgical Corporation experimented with the

liquid-liquid process of separation which involves the use of methyl isobutyl ketone (Coffer, 1958, p. 111).

Standard processing involves fused-salt electrolysis. A caustic soda fusion is followed by treatment by hydrochloric acid. Hydrofluoric acid and a potassium salt are added to form niobium potassium fluoride. Controlled cooling separates salts of niobium and tantalum at different temperatures (fractional crystallization). Niobium is prepared in commercial operations by reducing its oxide with niobium carbide, while tantalum is prepared by electrolysis of fused tantalum-potassium fluoride (Kauffman, 1957). The U. S. Bureau of Mines at Albany, Oregon, developed a new chlorination process for recovering niobium, tantalum, and other metals from western blacksands; this process, volatilization by chlorination, permits recovery of tantalum, niobium, and titanium chlorides. Uranium, thorium and rare earths are contained in the residues.

Other niobium-tantalum processing methods use hydrogen reduction and consumable-electrode arc melting (for the production of niobium ingots). Sintering in a high vacuum is perhaps one of the most common and best known of the current purification methods.

In the past prices of niobium and tantalum metal have been high due to periodic shortages and expensive processing techniques; however, new processes have aided price reduction.

Statistics for the period 1948-53 indicate that the United States produced only a little over 11.5 short tons of niobium-tantalum concentrates, chiefly from South Dakota, New Hampshire, Idaho, Connecticut, and Maine. Most of the ore was recovered as a by-product of other operations. During the 1944-53 period the United States imported an average of 1,304 short tons of columbite and 203 short tons of tantalite per year.

In July 1958, the U. S. Bureau of Mines Commodity Report for Region I noted that Mr. R. P. Porter, President of Porter Bros. Corp. of Boise, Idaho, urged greater domestic production of niobium and tantalum. In testimony before the Senate Interior Mineral Subcommittee, Mr. Porter suggested that the U. S. government should set up a purchasing program for 500,000 short tons of niobium-tantalum per year. From the production standpoint, he also indicated that at least 150 tons should be produced each year in order to operate a niobium-tantalum reduction plant efficiently and economically. The report implied that Porter Bros. Corp. were capable of supplying 200 short tons of niobium-tantalum product per year at that time.

Porter Bros. Corp. began work in 1955 in Bear Valley, Idaho. Production for that year was probably about 6 short tons of concentrate. Niobium and tantalum oxides, uranium oxides, rare earth carbonates, thorium concentrate, titanium concentrate, and other minerals also were obtained from Bear Valley placer materials (Fig. 1).

Barton (1958, p. 1-4) indicates that the total domestic production of niobium and tantalum concentrate reached a new high in 1956 and 1957, even though world production decreased. In 1956 approximately 107 short tons of concentrate were shipped from southeast Idaho. Through the period 1956-59, Porter Bros. Corp. produced approximately 185 short tons (around 98-99 percent of the total national production of concentrate) from Bear Valley placer deposits; however, production fell off in 1959 to about 95 short tons. When the U. S. government contract with Porter Bros. expired, the Bear Valley operation was suspended.

In 1957, the U. S. imported about 1,674 short tons of columbite, and 418 short tons of tantalite, principally from Nigeria and Belgian Congo. These figures indicate that domestic production accounted for only 8 to 9 percent of our columbite-tantalite requirements in 1957. The trend toward inadequate domestic production has apparently continued as evidenced by cessation of operations in Bear Valley and by the following statistical summary (Barton, 1959, p. 2).

Table 4

Niobium-tantalum domestic production
(short tons)

	<u>1956</u>	<u>1957</u>	<u>1958</u>	<u>1959</u>
Mine shipment:				
Nb-Ta concentrate (oxide content of euxenite plus total weight of Nb-Ta)	182	185	214	95
Imports:				
Nb-Ta concentrates	3,006	2,085	1,796	2,020

Barton (1959, p. 1) says:

Imports of columbium concentrates increased 33 percent. . . from 1958 to 1959. Imports of tantalum concentrates decreased 39 percent. . . within the same period. . . . Domestic production of columbium metal is estimated to have more than doubled in 1959, to a record high level. Tantalum metal production is believed to have increased more slowly. . . to an estimated record high of approximately 124 tons.

The goal is an ultimate market price of \$10-\$15 per pound or even less for high-grade niobium (Sims, 1958, p. 1). At the beginning of 1958, the price per pound for foreign ore containing 65 percent combined pentoxides was quoted at \$1.25-\$1.35 and \$1.05-\$1.15 for ratios of 10 Nb to 1 Ta, and 8.5 Nb to 1 Ta, respectively. By the year's end, these prices had dropped somewhat. Domestic prices, affected by

the buying program under U. S. Public Law 733 (84th Congress), remained at \$3.40 per pound of contained pentoxides (Barton, 1958, p. 2). In the first part of 1959 the prices quoted for niobium and tantalum were as follows (Eng. Mining Jour., 1959, p. 4):

niobium--rough ingots (99.5 percent) \$65-\$80 per pound;

tantalum - rod \$58 per pound
sheet \$45 per pound

Niobium is used as a ferroniobium and ferroniobium-tantalum in high temperature alloys. It also is used to stabilize stainless steel. Tantalum finds considerable use in electronics and corrosion resistant equipment. Niobium can be used in powder metallurgy to produce sheet, tube, rod, and wire products.

Earlier uses of niobium and tantalum included rectifiers for storage batteries (this use eliminated the old "B" battery), chemical and oxidation resistant alloys for instruments and apparatus, and alloys for use in high speed cutting tools. Niobium has been added to chromium and nickel steels to keep them ductile and to maintain their corrosion and oxidation resistance at moderately high temperatures. Tantalum, with an affinity for all common gases, is classed as a "getter." It has extensive application in the electronic tube industry.

Niobium in many respects is similar to molybdenum in its fabrication characteristics and behavior; however, the niobium has a low thermal neutron cross section and molybdenum does not. Niobium also has lower electrical and thermal conductivity, which is a disadvantage in applications where heat transfer is desirable. Yet, its strength is retained very well as temperature rises, which is a very desirable property.

Ogden (1958, p. 54-57) noted that niobium is ductile down to minus 100° C, and tantalum to minus 195° C. Good strength is maintained by these metals at temperatures as high as 815° C. Melting points are high: 1093° C for niobium, and 2850° C for tantalum. Thus, along with zirconium, they join the ranks of high-temperature-use metals.

Kauffman (1957, p. 9) reported the following companies most active in developing niobium and tantalum metals and in the production and promotion of their use:

Fansteel Metallurgical Corp., North Chicago, Ill., and
Muskogee, Okla.

Electro Metallurgical Division, Union Carbide and Carbon Corp.,
Niagara Falls, New York.

Kennametal, Inc., Latrobe, Pennsylvania.

Kawecki Chemical Co., Boyerton, Pennsylvania.
Wah Chang Corp., Albany, Oregon and Long Island, New York.
National Distillers Products Corp., New York, New York.
Mallinckrodt Chemical Works, St. Louis, Missouri.

A report issued later in 1958 (Eng. Mining Jour., 1958, p. 5) indicated that National Research Corp., Cambridge, Massachusetts, and U. S. Industrial Chemicals, Inc., Ashtabula and Cincinnati, Ohio, were beginning to produce niobium and tantalum metal. Stauffer Chemical Co., Richmond, California, began construction of a columbium and tantalum chlorides plant; and Temescal, Inc., began producing pure grade niobium ingots (1958).

According to Barton's report (1958), the U. S. Bureau of Mines niobium-tantalum research program for the 1959 fiscal year included investigation for cheaper methods of producing niobium and tantalum metals. Also, part of the program at Albany, Oregon, involved development of new alloys and compounds for use in nuclear reactors, guided missiles, jet engines, and electronic computers. New physical metallurgy studies will be started and the search for new domestic sources of raw materials will continue.

There should be an increase in future demand for niobium and tantalum as a structural material. In its pure form, tantalum resists corrosion by almost all acids which insures its extensive use in the chemical industry. Where strength at very high temperatures is required, niobium and tantalum metal should forge ahead, along with zirconium, as structural materials. Alloying should bring substantial improvements in this field. According to Ogden (1958, p. 56), niobium should be used more extensively in nuclear reactors because of its good strength and low cross section of neutron absorption.

Sherwood (1958, p. 1457) estimated that over 562 tons of tantalum would be required in 1960.

Extensive use of tantalum in glass-to-metal seals with sodium silicate promises to be a major contribution to the metal's industrial use and thus should increase the volume of metal consumed.

Thorium, scandium, yttrium, and the lanthanide rare earth metals

With similar chemical properties, the elements thorium, scandium, yttrium, and the lanthanide series are difficult to separate from each other. The periodic table of elements indicates that thorium is a member of the actinide (transuranium) group and is radioactive. These highly reactive elements in the actinide group include uranium, neptunium, plutonium, thorium, and several others that are less familiar.

Scandium and Yttrium occupy the same group position as the lanthanide and the actinides series. Little is known about scandium, but it seems to be somewhat similar to yttrium and the rare earths. More commonly found in minerals occurring

in basic rocks (rich in ferromagnesium components), scandium is not known to exist in any quantity in Idaho placer deposits.

Somewhat like aluminum in their properties, the rare earths are essentially basic in character, with basicities comparable to calcium. Rare earth salts differ from aluminum salts in that their degree of hydrolysis in aqueous solution is small. Some chemists prefer to separate the lanthanide or rare earth series into two groups as follows:

Table 5

Lanthanide or rare earth series

<u>Cerium group</u>		<u>Yttrium group</u>	
lanthanum	La	yttrium	Y
cerium	Ce	gadolinium	Gd
praseodymium	Pr	terbium	Tb
neodymium	Nd	dysprosium	Dy
promethium	Pm	holmium	Ho
samarium	Sm	erbium	Er
europium	Eu	thulium	Tm
		Ytterbium	Yb
		lutecium	Lu

It should be pointed out that yttrium is not technically one of the rare earth series.

Cerium is somewhat better known than lanthanum, but the latter should give its name to the series because it occurs earlier in the periodic table and is the first member of the rare earth series.

"Didymium" is the name Mosander gave to a substance derived from cerium. Believed to be a new element, didymium was later discovered to be a mixture of the elements praseodymium and neodymium. In practice the term "didymium" is applied to the mixture of rare earths left after cerium and thorium have been removed from monazite. Didymium, now a relatively inexpensive source of lanthanum, neodymium and other rare earths, has a composition approximately as follows:

Table 6

Composition of didymium

La ₂ O ₃	45.5%
Pr ₆ O ₁₁	11.0%
Nd ₂ O ₃	38.0%
Sm ₂ O ₃	4.0%
Other rare earth oxides and yttrium oxide	1.5%

Many of the minerals occurring in Idaho blacksands contain thorium, yttrium, and the lanthanide elements. In the field it is normally difficult or impossible to identify these rare earth elements separately.

Primary interest in thorium is now centered around its possible use as material for nuclear energy. For this reason, considerable interest has been aroused by the lode deposits of thorium in northern Idaho in the Hall Mountain area of Boundary County, and by those in the Agency Creek area of Lemhi County in eastern Idaho.

In some blacksand placers thorite constitutes a potential co-product of other heavy minerals and may eventually be of economic value; however, thorite in Idaho blacksand placers most commonly occurs in the form of the mineral monazite, which is widespread.

Thorium is not quite as plentiful in the earth's crust as lead and molybdenum, but it is more plentiful than uranium (Table 1a). It is found in the minerals allanite, bastnaesite, brannerite, eschynite, euxenite, monazite, polycrase, proritite, samarskite, thorite, and uranothorite. Up to 2 percent ThO₂ is found in many minerals as a partial replacement of rare earths. In the past, monazite has been exploited principally as a source of thorium.

Production of thorium salts from monazite sands involves the following steps:

1. gravity concentration from placer sands or bulk ore;
2. grinding and treatment with hot concentrated sulfuric acid;
3. and several stages of chemical treatment following ion exchange, and fractional precipitation of rare earth and thorium salts.

If metal is desired, the thorium oxide is reduced with calcium.

Though little has been done with thorium metal, it can be readily worked and fabricated. Thorium is produced chiefly in the form of nitrates and oxides but

metallic thorium is produced as rod, sheet, tube, fine wire, and foil products (U. S. Bureau of Mines, 1956, p. 878).

The melting point of metallic thorium is 1750° C, approximately the same as for titanium. Further research into this, and other properties of thorium metal should result in its broader application.

Radioactive thorium is a potential source of atomic energy. The use of thorium and U^{233} appears to offer excellent possibilities for breeding or, at any rate, for achieving high conversion ratios in nuclear reactors. There are physical advantages to the use of thorium in place of uranium: thorium metal can withstand much higher temperatures than uranium metal, thorium has a higher thermal conductivity rate, and recently it was demonstrated that thorium fuels are more resistant to radiation damage than are uranium metal products. However, major technological problems in the use of thorium in nuclear reactors remain to be solved. In the United States experimental reactors and full scale reactors are using (or investigators are planning to use) thorium metal as fuel.

One producer in 1954 quoted prices for several thorium products as follows (U. S. Bureau of Mines, 1956, p. 880):

Table 7a

Prices of thorium products	
<u>Price per gram for 200 or more grams</u>	
Powder	\$0.35
Unsintered bars	0.40
Sintered bars	0.50
Sheet, 0.005 inch and over.....	0.60
<u>Price per pound for 100-pound lots</u>	
Thorium nitrate, mantle-grade.....	\$3.00
Thorium oxide, 97 percent ThO_2	8.25
Thorium oxide, photographic lens-grade 99 percent ThO_2	9.35

Lewis (1960, p. 2) quoted prices as follows: "Prices on domestic monazite and thorite concentrates varied from about \$170 to \$210 per short ton, depending upon the percentage of contained REO (rare earth oxides) and/or ThO_2 ". Lindsay Chemical Division, American Potash and Chemical Corp., quoted the following prices for thorium products in February 1961:

Table 7b

Prices of thorium nitrate, oxide, and chloride

Thorium nitrate, mantle grade.....	\$3.30-\$5.40 per pound
Thorium oxide.....	\$6.88-\$11.25 per pound
Thorium chloride	\$7.70-\$12.60 per pound

Principal producers of thorium products from monazite and other thorium minerals are:

- Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Illinois.
- Maywood Chemical Works, Maywood, New Jersey.
- Davison Chemical Division, W. R. Grace Co., Curtis Bay, Maryland, and Pompton Plains, New Jersey.
(Includes former Rare Earths, Inc.)

Because thorite minerals have been regulated under the Atomic Energy Act of 1954, production figures are difficult to obtain; however, Kauffman (1957, p. 13) states that about 47 short tons of ThO_2 were consumed in 1956 for non-energy purposes. Domestic production of monazite is chiefly from placer sands in Idaho, Florida, and the Carolinas.

Non-energy use of thorium is primarily as thorium oxide containing one percent cerium oxide. This mixture emits a very brilliant light when heated to incandescence. It is the basis of the incandescent gas mantle devised by Welsbach for kerosene lamps and gasoline lanterns. Other non-energy uses for thorium and its compounds are:

- catalyst for petroleum industry;
- catalyst for chemical industry;
- optical glass;
- medical uses: creams, lotions, pastes, and powders;
- refractories (thoria has melting point at $2,800^\circ\text{C}$);
- additive to magnesium alloy to improve temperature properties;
- electronic applications (a "getter," i.e. has affinity for gases);
- and polishing compounds.

The future of monazite from Idaho blacksands probably depends largely upon continued research and development of thorium for non-energy uses; use as nuclear reactor material for producing atomic energy and use of Idaho's lode thorite deposits, and other sources of supply. The demand for co-product detrital minerals in the black-sand placers will also influence any future development of Idaho monazite. Production of a combination of mineral products in this fashion might put Idaho placers in a position to compete successfully with California bastnaesite, which is principally only a source of rare earths.

Yttrium and the lanthanide series (rare earths) are plentiful in the earth's crust, as plentiful as copper, lead, and zinc (Table 1a). Over 200 minerals are known to contain appreciable amounts of these "rare" elements, including allanite, cerite, monazite, euxenite, bastnaesite, brannerite, cyrtolite, fergusonite, hjelmite, polycrase, priorite, samarskite, xenotime, and gadolinite. Rare earths in "pure" monazite may constitute from 45 to 68 percent of the mineral by weight. Kauffman (1957, p. 12) reports that a total of 1,950 short tons of rare earth oxides was produced from domestic monazite and bastnaesite in 1956.

Considerable monazite ore has been imported from India and Brazil, but embargoes were placed on these sources in 1947 and 1951. Imports have also come from the Union of South Africa.

The U. S. Bureau of Mines (1956, p. 735) states that California bastnaesite deposits are "...capable of supplying all of the foreseeable raw-materials requirements of the United States for the production of rare-earth metals and compounds." If the demand for thorium increases appreciably in the future, however, rare earths will probably be produced as a co-product from minerals containing a variety of valuable metallic products.

Concerning the production and consumption of monazite ore, Ransohoff (1958, p. 2) says:

...current consumption of monazite ore is on the order of 10,000 tons per year... (averages about 6 percent ThO_2 and 45 percent rare earth oxide). For each ton of thorium processed, about 7 tons of cerium group rare earths not of interest will be produced... potential yield of the other rare earths would be 300 pounds of yttrium, 300 pounds of samarium, 60 pounds of gadolinium, 15 pounds of dysprosium, 8 pounds of erbium, and about 3 pounds of europium.

The rare earths and yttrium are all produced by preliminary gravity concentration followed by sulfuric acid treatment to produce sulfates. These are converted to pure salts by fractional crystallization and ion-exchange methods. Metals are produced by electrolysis of the fused chlorides.

Because individual rare earth elements are difficult to separate, the rare earths are used in the form of misch metal in some applications. Misch metal is a mixture of the rare earth elements, roughly as they occur naturally; for example, the following percentages are common in misch metal:

cerium, 50 percent	samarium, 1 percent
neodymium, 18 percent	lanthanum and others,
praseodymium, 5 percent	24-26 percent

The salts of cerium, lanthanum, and neodymium seem to be in greatest demand at the present. Rare earth chloride, the salt of misch metal, is now available for commercial use. In addition to cerium, misch metal and pure metal forms of rare earths are also used in ferrocerium, an alloy of misch metal and approximately 25 percent iron.

Recently, the U. S. Bureau of Mines released a report on progress in the development of commercial-grade yttrium metal (U. S. Bureau of Mines, 1959, p. 1-2). Using a modification of the Kroll process, pliant and ductile yttrium metal of high purity may be obtained. Yttrium metal can now be cold-rolled into very thin foil. The metal has a relatively high melting point (1551° C) which will enable it to withstand the range of temperatures encountered in atomic reactors and atom-powered propulsion engines (e.g. missiles and rockets); and it has a relatively low cross section for thermal neutrons, which is important where a chain-reaction is to be sustained over long periods of time.

The cost of yttrium metal is quite high, even with the present processing method; however, further refinements may come, and with the possibility of increased demand, prices should drop.

Rare earths in general are still costly. The following table is a summary of prices quoted for various products (adapted from Himes, 1958, p. 3):

Table 8a

Prices of rare earths

<u>Material</u>	<u>1948</u> (dollars per pound*)	<u>1958</u> (dollars per pound*)
Misch metal	4.00	3.00
Cerium metal (98%)	50.00	
Gadolinium metal (?%)	--	350.00
Dysprosium metal (?%)	--	350.00
Neodymium oxide (99%)	77.00	50.00
Yttrium oxide (99.0%)	1,135.00	158.00
Praseodymium oxide (99.9%)	1,362.00	113.50
Samarium oxide (99.9%)	3,178.00	113.50
Gadolinium oxide (99.9%)	18,160.00	249.70
Europium oxide (99%)	181,600--385,900	908.00
Thulium oxide (?%)	1,271,200.00	6,060.90

*Note: Neodymium to thulium: prices are normally quoted for one gram lots, but for comparative purposes figures are here converted into price per pound, using gram lot quotations. However, quantity lots generally sell for proportionally less than smaller quantities.

The following prices in terms of dollars were quoted by the Lindsay Chemical Division of American Potash and Chemical Company (February, 1961):

Table 8b

Prices of rare earth oxides
(one pound lots)

<u>Material</u>	<u>Grade 99 percent</u>	<u>Grade 99.9 percent</u>
Neodymium	\$ 35	\$ 40
Praseodymium	40	50
Samarium	50	60
Europium	750	908 (99.8%)
Gadolinium	105	125
Terbium	850	900
Dysprosium	105	125
Erbium	105	125
Yttrium	70	80
Holmium	105	125
Ytterbium	160	200
Thulium	850	900
Lutecium	1,200	1,500

Prices quoted by the same company for cerium and lanthanum oxides were:

Table 8c

Prices of cerium and lanthanum oxides

Ceric oxide (purified).....	\$ 9.00 per pound (99.9+%)
Lanthanum oxide (purified)	\$10.55 per pound (99.97%)

Major domestic producers of rare earths are:

- Lindsay Chemical Division, American Potash and Chemical Corp.,
West Chicago, Illinois
- Maywood Chemical Works, Maywood, New Jersey
- Davison Chemical Division, W. R. Grace Co., Curtis Bay, Maryland,
and Pompton Plains, New Jersey
- General Cerium Corp., Edgewater, New York
- New Process Metals Division, Ronson Metals Corp., Newark, New
Jersey
- Cerium Metals and Alloys Division, Ronson Metals Corp., New
York, New York

American Metallurgical Products Co., Pittsburgh, Pennsylvania
Mallinckrodt Chemical Works, St. Louis, Missouri
Molybdenum Corporation of America, New York, New York

The following summary of uses for rare earths is indicative of their growing broad use base in various industries:

Electrical, electronic, and nuclear applications

carbon-arc lighting, motion picture projection, color TV tubes, fluorescent lighting phosphors, electronic equipment, neutron absorbers in nuclear reactors

In alloys

stainless steel, medium and low-carbon steel, alloy steel, aluminum alloys, lighter flints, rare earth-zirconium-magnesium alloys

In ceramics

flame-sprayed coatings, opacifiers, colorizers

In glass

glass coloring; glass decolorizing; polishing of lenses, mirrors, TV picture tubes and implosion plates, quartz crystals, semi-precious stones and other materials; photosensitive glass; glass windows for radiation protection; and sun glasses, glass blowers' glasses and welders' goggles

In the chemical industry and miscellaneous uses

catalysts and reagents; textile waterproofing; scavenger in explosives manufacture; paint driers; nausea preventitive.

In 1956, about 25 percent of the total consumption of rare earths was for carbon-arc electrode cores in lighting. In the electronic and electrical field special ferromagnetic properties have been recognized in rare earth-iron garnets. Himes (1958, p. 3) comments:

The low electrical conductivities and low eddy-current losses of these garnets made them especially valuable as magnetic-core materials in microwave and television applications... yttrium-iron garnet has shown greatest promise to date.

Himes points out that some of the rare earths have superconductivity at very low temperatures, making them potentially useful for building "memory" and control devices that operate at very low temperatures.

There is no question about the versatility of the rare earth elements. For example, during World War II, ceria was used instead of rouge for polishing lenses, prisms and other optical equipment. Cerium is also a valuable oxygen carrier and catalyst. Niodymium is used in the glass industry and the electronics industry. Lanthanum, as a base with other oxides, produces a glass of high density, with a high index of refraction and low dispersion. Photographic lenses made with lanthanum during World War II were remarkable in performance (Hammond, 1946, p. 2).

Rare earths have potential as activators in phosphors and will probably be used in growing quantities in television and modern lighting, and in the construction of electron emitters of several types. The rare earths also are good gas scavengers ("getters"). The fairly recent use of rare earths in solar-energy-type batteries shows considerable future promise, particularly in space travel applications.

In the nuclear field, control rods and neutron shields containing samarium, gadolinium, europium, dysprosium, and erbium show promise as shielding material. Their extremely high cross-sections provide a successful barrier to neutron passage. These materials are still expensive, but only because of the cost of separation, not rarity, in the earth's crust. Production will increase and separation techniques should improve, resulting in lower costs.

Yttrium, with one of the lowest neutron-absorption cross sections, offers great promise for structural material. Its relatively high melting point and low density (Table 1a) may serve to advance yttrium as a valuable building material in the development of atomic power.

In ceramics fairly large quantities of cerium oxide and mixed oxides are going into polishing agents. Yttrium oxide (melting point, 2400° C) and the borides and carbides of several of the rare earths are high-temperature refractories.

Light rare earths are being alloyed successfully with magnesium and aluminum, as well as with steel. Also, potential applications of rare earths in high-temperature metals seem assured. As catalysts, the rare earths may offer competition to such well-known elements as palladium, thodium, and platinum (Himes, 1958, p. 6).

There is much speculation concerning the future of the rare earths. While some of the proposed uses seem reasonable, some appear fanciful; the single most important factor seems to be versatility of these rare elements. Their similarity to each other, and also their similarity to the other heavy metals, should become major factors in any increased usage.

Domestic capacity for production of rare earth commodities is growing, use is expanding, and prices are falling; these are good economic indicators. Domestic supplies appear adequate for market expansion, particularly as the several metals may be exploited in multiple operation, co-product and by-product operations. The impetus of missile building and international competition in research, brings metallurgy to an era of new products for the space age, in which rare earths should assume an important position. Together, they may overshadow some of the better known "work horse" minerals and elements.

Kauffman made the following statement (1957, p. 16):

...revitalization of monazite mining in Idaho would seem to depend upon a change in the thorium-requirements picture or cessation of imports due to the world situation. One possible exception would be development of a strong market for either, or both, the associated zircon and ilmenite found in the Idaho sands.

Revitalization of metal mining in Idaho must depend upon recognition of the current trend in metallurgical requirements, recognition of multiple mineral production techniques, and development of breadth and depth in the use of "minerals of the future."

As for future metal price reductions, Lindsay Chemical Division, American Potash and Chemical Corp., (Lindsay Chemical Division, 1958, p. 1) issued this statement:

Costs for rare earth metals depend on the cost of the rare earth material, the cost of separation, the scale of operation, and to some extent the purity produced. The ultimate costs in quantities may compare with those for titanium and zirconium. Eventually, the more abundant rare earth metals might cost \$5 to \$20 per pound.

OUTLOOK

The future for metals developed from blacksand minerals should be good; however, the picture is not yet sufficiently clear to permit a prediction as to which minerals will be used in volume. Technological hurdles remain, but research is continuing and early results appear favorable to a solution of many problems. Stuart (1960, p. 7) comments appropriately:

In the future, as now, the market for many of the alloys developed for missiles, will continue to be small. But, as alloys are developed, resourceful materials-application engineers will find economic uses for them in industrial fields as well, and the entire economy will benefit. . . . The full impact of this research on our general technology will not be felt for many years.

While research continues, Idaho blacksands, for the most part, "lie fallow," but meanwhile we are learning about their location, mineral content, and volume. Briefly, we know something about what we have, but we must await further progress in metallurgy and the concurrent development of a metal market to make possible the exploitation of a sizeable mineral resource: blacksand placers.

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