Thorium

By Roman V. Sondermayer [1]

As in the past, there was no direct mine production for thorium as such during 1972, and demand for thorium was not the decisive factor in determining its supply. Production of thorium was essentially a byproduct of the monazite operations for rare earths. Consequently, there was a continuing and excessive stock of thorium-bearing raw materials. The weak market continued, but the long-term potential for use of thorium was considered good. Demand for thorium hardener, used in magnesium alloys for aerospace applications, increased slightly. New orders for thorium-uranium-fueled high-temperature, gas-cooled reactors (HTGR) improved the long-range demand potential for thorium nuclear fuels. Continuing research may introduce new industrial applications for thorium and its compounds in metallurgy and nuclear fuels, thus resulting in larger consumption of thorium.

The most significant events related to thorium during 1972 were the beginning of a new beach-sand (containing monazite) operation in Florida, the preliminary accord for the sale of two HTGR's to Southern California Edison Co., and the participation of Gulf General Atomic Co. (GGA) in construction of a HTGR in West Germany.

Legislation and Government Programs.—The entire inventory of thorium held by the Government was authorized for disposal. However, there was no response to the request for bids during 1972, and thorium and its compounds were not sold from the stockpile. At the end of 1972, 1,789 tons of thorium-oxide (ThO_2) equivalent were held by the Government in stockpile.

Effective January 1, 1972, under the "Kennedy round" schedule of tariff reductions, ad valorem duties were reduced to 17.5% on thorium compounds, 6% on metal, and 7.5% on thorium alloys.

DOMESTIC PRODUCTION

Mine Production.—Production of byproduct monazite from a Pleistocene beach-sand deposit, located 35 miles inland and 10 miles fron Green Cove Springs, Fla., started in October 1972. Titanium Enterprises, jointly owned by American Cyanamid Co. and Union Camp Corp., became the second domestic monazite producer. In addition to monazite, mine products included ilmenite, leucoxene, rutile, and zircon.

Humphreys Mining Co., with its operation near Folkston, Ga., remained the largest producer of monazite in the country. Output was slightly lower in 1972. Estimated ThO_2 content remained at 5%. Heavy-mineral sands were mined by suction dredge for their titanium minerals and zircon content. The byproduct monazite was sold under contract to W. R. Grace & Co., Chattanooga, Tenn. Monazite was processed essentially for its rare earths oxide (REO) content. Thorium-bearing residues were stockpiled for processing as needed.

Humphreys Mining Co. continued land rehabilitation of an area disturbed by mining. Mill waste was used as fill, and, after grading, topsoil was respread, fertilized, and planted with grass. The company was presented with the State of Georgia first honor award for land reclamation achievements.

Refinery Production.—The principal domestic firms processing monazite for

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[1] Physical scientist, Division of Nonferrous Metals.

rare-earth elements and thorium were W. R. Grace & Co., at Chattanooga, Tenn., and Lindsay Rare Earths, affiliated with Kerr-McGee Chemical Corp., West Chicago, Ill. A number of thorium-processing companies maintain stocks of various compounds and the metal for nonenergy use and for nuclear fuels.

Table 1.—Companies processing and fabricating thorium, 1972

Company	Plant location	Operations and products
American Light Alloys, Inc	Little Falls, N.J	Magnesium-thorium alloy.
Consolidated Aluminum Corp	Madison, Ill	Do.
Controlled Castings Corp	Plainview, N.Y	Do.
Gallard-Schlesinger Chemical Manufacturing Corp.	Carle Place, N.Y	Processes oxide, fluoride, and metal.
General Electric Co	San Jose, Calif	Nuclear fuels.
Do	Wilmington, N.C	Do.
W. R. Grace & Co., Davison Chemical Div.	Chattanooga, Tenn	Processes domestic and imported monazite; produces oxide; stocks of hydroxide and metal powder.
Gulf General Atomic Co	San Diego, Calif	Nuclear fuels.
Gulf United Nuclear Fuels Corp	Hematite, Mo	Do.
Do	New Haven, Conn	Do.
Hitchcock Industries, Inc	South Bloomington, Minn.	Magnesium-thorium alloys.
Kerr-McGee Chemical Corp	Cimarron, Okla	Nuclear fuels.
Lindsay Rare Earths	West Chicago, Ill	Processes imported monazite; stocks of thorite; produces oxide, nitrate, and oxalate.
NL Industries, Inc	Albany, N.Y	Nuclear fuels.
Nuclear Chemicals and Metals Corp	Huntsville, Tenn	Do.
Nuclear Fuel Services, Inc	Erwin, Tenn	Do.
Nuclear Materials & Equipment Corp. (NUMEC).	Apollo, Pa	Do.
Do	Leechburg, Pa	Do.
Ventron Corp., Chemicals Div	Beverly, Mass	Metallic thorium.
Wellman Dynamics Corp	Creston, Iowa	Magnesium-thorium alloy.
Westinghouse Electric Corp	Bloomfield, N.J	Processes compounds; produces metallic thorium.
Do	Columbia, S.C	Nuclear fuels.

CONSUMPTION AND USES

Based on monazite production and foreign trade figures, apparent consumption of thorium (in terms of ThO_2 equivalent) was estimated at 300 tons during 1972. However, actual domestic industrial consumption was lower because the monazite supply was processed for its rare earth content, and most of the thorium residue remained in company holding areas.

Nonenergy industrial consumption was estimated at 100 to 150 tons ThO_2 equivalent. The major uses were in incandescent gas lamp mantles; hardener for magnesium-thorium alloys in aerospace applications; dispersion hardening of metals such as nickel, tungsten, and stainless steel; and electronic, refractory and chemical (catalytic) applications.

In the nuclear field, research and development studies continued on thorium-uranium fuels, reactor concepts for these fuels, and thorium fuels reprocessing. Thorium-uranium fuels (Th_{232}-U_{232} fuel cycle) are used in the HTGR, the molten-salt breeder reactor, and seed-blanket loadings for the pressurized water reactor.

During 1972, plans for construction of two HTGR nuclear power plants were announced. The Southern California Edison Co. signed a letter of intent with GGA, of San Diego, Calif., a Division of Gulf Oil Corp., to design and supply two 770,000-kilowatt HTGR's to be located in the eastern California desert. A site for the facility had not been selected at yearend. The first unit was tentatively scheduled for operation in 1981. Southern California Edison has also taken an option for two additional, larger capacity HTGR units that would be located at another site.

A second HTGR plant was planned by Delmarva Power and Light Co., Wilmington, Del. The new nuclear power station will consist of two 700,000-kilowatt HTGR's, and the total costs were reported to be $680 million. The site is located 15 miles south of Wilmington. Reportly, the first unit would be operational in 1979, and the second one 2 years later. GGA will design and supply the HTGR's.

Table 2.—U.S. foreign trade in thorium and thorium-bearing materials

(Quantity in pounds unless otherwise specified)

	1970		1971		1972		Principal sources and destinations, 1972
	Quantity	Value	Quantity	Value	Quantity	Value	
EXPORTS							
Ore and concentrate (ThO₂ content)	81	$1,296	--	--	--	--	
Metals and alloys[1]	5,503	86,021	65,592	$943,930	16,624	$291,048	Italy 14,119; Canada 1,695; Japan 554.
Compounds[1]	4,045,549	24,579,293	6,021,148	38,498,069	6,714,148	46,614,501	Canada 4,170,598; United Kingdom 2,521,235.
IMPORTS							
Ore and concentrate:							
Monazite (short tons)	3,448	427,411	3,373	383,733	894	$88,767	All from Malaysia.
ThO₂ content[e]	413,800	--	404,800	--	107,300	--	
Waste and scrap	--	--	--	--	15	285	All from Canada.
Compounds:							
Nitrate	5	382	1,100	1,891	4,502	15,612	All from France.
Oxide	10	280	2,481	8,692	317	1,833	France 290.
Oxide equivalent, in gas mantles[e] [2]	4,100	409,110	5,900	618,616	5,804	539,558	United Kingdom 2,795; Austria 1,000; Malta 692; Italy 600; West Germany 464.
Other	252	23,253	227	28,195	151	22,811	Switzerland 118.

[e] Estimate.

[1] Includes uranium; thorium and uranium are undifferentiated in official statistics.

[2] Based on manufacture of 1,000 gas mantles per pound ThO_2.

FOREIGN TRADE

During 1972, imports of monazite largely for the rare earth content, decreased sharply (83.5%) from 1971 levels. Malaysia was the only supplier of monazite during 1972. Imports from Australia, the largest supplier in 1971, ceased during 1972. Imports of thorium oxides decreased significantly (87%), but imports of thorium nitrate were about four times higher than in 1971. These compounds were imported from France. Imports of gas mantles decreased slightly (1.6%) from 1971 levels. The United Kingdom and Austria were the principal suppliers.

Minor imports of thorium waste and scrap were registered during 1972 for the first time since 1970.

In official statistics, thorium and uranium exports are undifferentiated. Consequently, it is impossible to evaluate thorium exports only. However, the composite figure for thorium and uranium exports indicated a decrease in metal and alloy exports and an increase in exports of compounds.

WORLD REVIEW

Australia, India, Brazil, Malaysia, and the United States were the principal world producers of monazite concentrate, the main source of thorium, during 1972. No raw material was mined for recovery only of ThO_2; output of monazite and ThO_2 resulted from operations of the rare earth industry.

Brazil.—During 1972 no major changes were reported in the beach sand industry. The Commissão Nacional de Energia Nuclear (CNEN) controlled the overall production of monazite in the country. CNEN, through Administração da Produção da Monazita (APM), operated workings at Itabapoana (Rio de Janiero) and Cumuruxatiba (Bahia). Monazita e Ilmenita do Brasil (MIBRA), a privately owned company, operated facilities for the production of monazite at Guarapari.

Law 5740, enacted in December 1971, created a mixed Government-private company, Cia. Brasileira de Tecnologia Nuclear (CBTN), to operate under CNEN in certain commercial aspects of nuclear energy. The stated objectives of CBTN were reported as follows: to prospect for and mine nuclear and associated mineral deposits through the Cia. de Pesquisa de Recursos Minerais (CPRM), and the development of nuclear energy and its uses. CBTN will have headquarters in Brasilia, the company's capital will amount to $18 million. The law stipulates that only Brazilians can be directors and members of the fiscal council of the company.

Canada.—There has been no thorium production since 1968, although large thorium resources exist in Canada. Some

Table 3.—Monazite concentrate: World production by country

(Short tons)

Country [1]	1970	1971	1972 p
Australia	4,891	4,854	5,537
Brazil	2,544	1,502	2,453
India [2]	4,004	4,664	e 4,700
Malaysia [3]	1,827	1,621	1,927
Mauritania e	110	110	110
Mozambique	2	—	—
Nigeria	14	102	11
Sri Lanka (formerly Ceylon)	18	7	e 10
Thailand	119	123	188
United States	W	W	W
Zaire	158	239	e 240
Total	13,687	13,222	15,176

e Estimate. p Preliminary. W Withheld to avoid disclosing individual company confidential data.

[1] In addition to the countries listed, Indonesia and North Korea produce monazite, but information is inadequate to make reliable estimates of output levels.

[2] Year beginning April 1 of that stated.

[3] Exports.

research continued to reduce costs and produce high-purity thorium.

In addition, authorities prepared detailed proposals for legislation regulating ownership in the nuclear industry. At yearend, no information was available on the status of this legislation.

Germany, West.—During 1972, Gulf Energy and Environmental Systems Inc. (GEES) acquired a 45% interest in Hochtemperatur Reaktorbau GmbH (HTR); Brown, Boveri and Co., Mannheim, retained 55% interest in the new company. GEES as part owner will license HTR to use GGA-developed HTGR technology. In return, GEES would gain access to the technology of the thorium high-temperature reactor (THTR) with its "pebble bed" fuel concept that HTR expects to demonstrate in a prototype reactor at Schmehausen, near Dortmund.[2]

India.—According to Indian Rare Earths Ltd. (IRE), monazite production increased nearly 7% during the fiscal year ending March 1972.[3]

Production and sales data for fiscal 1971 and 1972 were as follows, in short tons:

	1971 [1]	1972 [1]
Monazite processed	3,903	4,165
Production of thorium hydroxide	1,378	1,499
Sales of monazite:		
Quantity	3,745	4,677
Value ---------- thousands	$147	$181
Sales of thorium hydroxide [2] -- do	$68	NA

[1] Fiscal year ending March.

[2] To Indian Government.

The IRE will make a feasibility study of the mineral sand deposits along the Orissa coast for assessing the monazite content. Mineral sands are found near Gopalpura, on a 25-mile stretch of the Orissa coast. If results of the study are favorable, IRE plans to build a mineral separation plant in Orissa. IRE also planned to double the capacity of the Chavara mineral sand plant in Kerala State from 110,000 to 220,000 short tons per year and to expand capacity of the Manavalakurichi plant from 55,000 to 88,000 short tons per year. The company continued to operate the thorium plant at Trombay as agent of the Government of India.[4] The company also discussed with the Department of Atomic Energy and Bhabha Atomic Research Center the details of a program of scientific cooperation with the Center for Research and Development at Trombay.

Indonesia.—The State-owned Perussahaan Negara Tambang Timah planned to extract monazite as a byproduct of tin mining. Expansion of facilities to increase tin production and separate marketable monazite concentrates was reported.[5]

Sri Lanka (formerly Ceylon).—The Ceylon Mineral Sands Corp. announced plans to expand its mineral sand facility at Pulmoddai. Equipment from the China Bay plant will be dismantled and used for the expansion. Upon completion, the new integrated sand complex at Pulmoddai will have an annual capacity of 200,000 tons of raw sand yielding 500 tons of monazite and other products. During 1972, a special committee representing the Ministry of Industries, Ministry of Irrigation, and others was formed to ensure timely construction of ancillary facilities for the project.[6]

South Africa, Republic of.—During 1972, two discoveries of monazite were reported The first indicated monazite reserves in sand dunes near Garies, Namaqualand. A concentration of heavy minerals was first noticed by airborn radiometric survey. Reserves were reported at 95 million tons of sand with a 10% content of heavy minerals. The second discovery was in the northeastern Transvaal, 56 kilometers north of Rustenburg. Production of thorium as a byproduct may be possible. Assays indicated an average content of 3.16% ThO_2.[7]

Although the heavy minerals recovery plant of Palabora Mining Co. Ltd. at Phalaborwa, Transvaal, went on stream in 1971, technical details of the operation were not reported until 1972. Tailings from the copper concentrator are used as the raw material for heavy minerals production. The six modules of the heavy minerals plant correspond to the six sections of the copper concentrator. After desliming and removal of magnetite, the entire tail-

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[2] Atomic Industrial Forum. New German Link Strengthens Gulf's European HTGR Alliances. Nuclear Ind., v. 20, No. 1, January 1973, pp. 36–37.

[3] Indian Rare Earths Ltd. 22nd Annual Report 1971–72, Bombay, 1972, pp. 32.

[4] Engineering and Mining Journal. V. 174, No. 1, January 1973, p. 148.

[5] American Metal Market. Ore Deposits in Indonesian Waters. V. 79, No. 139, July 28, 1972, pp. 14–15.

[6] Ministry of Industries. Review of Activities of Corporations 1971–72, pp. 53–57.

[7] South African Mining and Engineering Journal. Important Rare Earth Deposits in the Pilensburg. V. 84, No. 4068, May 1972, pp. 13–15.

ings output of the concentrator is processed through the plant. About 22,000 tons per day of dry solids represents the average quantity fed to the plant. Uranothorianite concentrate, obtained by gravity concentration and containing approximately 5% U_3O_8, 14% ThO_2, and 65% ZrO_2, was processed through the chemical extraction plant. Thorium and uranium are extracted by leaching with hot nitric acid. The liquor containing thorium and uranium is then treated in a solvent extraction circuit and the product calcined. A new feature of the process is the provision of facilities for recovery of nitric acid and thorium from the barren solution or raffinate from the solvent extraction. Since the ThO_2:U_3O_8 ratio is on the order 2.5:1, thorium could become an important byproduct.[8]

United Kingdom.—The United Kingdom Atomic Energy Authority won a contract to design and supply a solid moderator reactor (SMR) for the THTR under construction at Schmehausen in West Germany. The function of the SMR is to facilitate reloading of the THTR.[9]

Venezuela.—The Government announced a discovery of thorium in the Cerro Impacto Codesur area of southern Venezuela. The area was reserved for exploration by the State through a Government-owned corporation called Promocion Del Desarrollo Del Sur de Venezuela (Prodesur). Information on size of deposits and reserves was not reported.

TECHNOLOGY

Energy and metallurgical applications together with extraction techniques were the principal subjects of studies related to thorium during 1972. Most of the research was basic, and industrial utilization of results was not imminent.

Nonenergy.—At the Elliot Lake uranium mine in Ontario, Canada, large volumes of waste materials contain thorium. An investigation was conducted to find a solvent extraction process for the coextraction of uranium and thorium. The new approach would replace the present precipitation procedure for thorium elimination, which is costly because of neutralization and coprecipitation losses of the rare earths. Results indicated that high-purity thorium sulfate can be produced with the ion exchange-neutralization route. In addition, increased revenue would result if thorium is recovered.[10]

Metallurgical research was directed toward studies determining the effects of thorium and thorium compounds on physical and chemical properties of alloys, mostly high-temperature alloys, in different environments. One investigation indicated that addition of ThO_2 to high-temperature nickel or cobalt-base superalloys slows oxidation. In an oxidation process induced by Na_2SO_4, the presence of ThO_2 in a nickel-chromium alloy promoted selective oxidation of chromium, and the growth rate of the chromium oxide layer was approximately one order of magnitude less than that for growth of chromium oxide in simple nickel chromium alloys.[11]

The application of fine wires as high-strength structural components requires a better undertanding of differences of creep behavior. The creep properties of fine, recrystallized tungsten-thorium oxide (1% ThO_2 by weight) wires were studied over the temperature range 1,800° to 2,750° C. The creep behavior of tungsten-thorium alloy wire depends on grain structure, temperature, and stress. The study showed that the creep behavior of fine wires was not affected by geometry, and identical results could be expected for larger diameter specimens.[12]

Ronson Metals Corp.'s "CerAlloy 400," made of approximately 80% thorium, 15 mischmetal, and 5% aluminum, was used in plutonium-powered pacemakers (small devices, surgically implanted in body, regulating the rhythm of heart beat). The new pacemaker should operate for 10 years

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[8] Nel, V. Palabora's New Heavy Minerals Plant Adds Uranium Concentrate to the Recovery List. Eng. and Min. J., v. 173, No. 11, November 1972, pp. 186–187.

[9] Chemistry and Industry. UKAEA Win Reactor Contract. No. 3, Feb. 5, 1972, p. 104.

[10] Ritcey, H. C., and B. H. Lukas. Co-extraction of Uranium and Thorium. J. of Metals, v. 24, No. 4, April 1972, pp. 39–44.

[11] David, H. H., H. C. Graham, and G. F. Uhlig. Oxidation of Na_2SO_4-Coated Ni-20Cr-2ThO_2. Met. Trans., v. 3, No. 12, December 1972, pp. 3247–3257.

[12] Moon, D. M. Creep of Fine Wires of W-ThO_2 Alloys. Met. Trans., v. 3, No. 12, December 1972, pp. 3097–3102.

without change of power source, which is now necessary every 30 months.[13]

A dispersion-modified alloy containing thorium with nickel and chromium was under development for use in the space shuttle. Necessary properties of this alloy are high-strength, formability, and good oxidation resistivity at 2,200° F. Research indicated that a 2% to 5% addition of aluminum to the base alloy improved the oxidation resistance of the basic Ni-Cr-ThO system with a loss of strength at elevated temperatures.[14]

Th-Ni systems were studied over a composition range from 50% to 96% Ni and a temperature range of 1,000° to 1,500 C. Intermetallic compounds were observed that were not previously found. Alloys in this composition range were stable in air. A few alloys were annealed for 14 days at 800° C. Th-Ni alloys showed some similarities to Th-Si alloys.[15]

Work on optical absorption spectroscopy of ThO_2 was extended to purer specimens than those used previously. The fundamental absorption edge for these specimens lies at much higher energy than the apparent edge reported previously. A full analysis of certain crystals by spark-source mass spectrometry indicated that no strong correlation existed between specific band areas and impurity-element concentration. Moreover, purer specimen of fused ThO_2 revealed new, previously unobserved bands of the ThO_2 spectrum.[16]

Behavior of thorium-carbon alloys in a nitrogen environment at moderate pressures was examined. Results indicated an "uphill" (up a concentration gradient) diffusion of carbon in the ternary solid solution Th(C,N). This explains the tendency for carbon and thorium to segregate in the course of reaction of thorium carbon alloys with nitrogen at moderate pressures.[17]

Energy.—Effects of additives on the sintering of ThO_2 and ThO_2-Y_2O_3 compacted and loose powders were studied. The investigation showed that small amounts of nickel oxide are potent and increase the rate of sintering of thorium oxide, and the major portion of densification occurs very rapidly and is followed by a much slower process of sintering.[18]

A new HTGR concept was under investigation. GGA of San Diego, Calif., negotiated a contract with the Atomic Energy Commission (AEC) for design, engineering, and construction of a nuclear gas-turbine powerplant, which would eliminate the steam-turbine cycle by combining the HTGR with a closed-cycle helium gas-turbine generator. Hot helium at 1,500° C would turn the gas-turbine generator. Benefits of the new concept include savings in capital costs, improved reactor operating efficiency, and reduced environmental impact since lesser quantities of cooling water are needed.

The light water breeder reactor (LWBR) fuel is ThO_2 pellets in which 1% to 6% U_{233} in UO_2 form is dissolved. A project was underway to develop a chemical flowsheet for converting uranium-nitrate solution to ceramic grade UO_2 powder having desired properties for uniform blending with ThO_2 powder and for pressing and sintering to high-density fuel pellets for the LWBR.[19]

Solvent properties and corrosiveness of liquid sodium, which is used as a coolant in fast-breeder reactors, were the subjects of a study originating in Sweden. A system of corrosion in liquid metals is often accompanied with mass transfer of corrosion products, and alloys form within the bulk phase of the liquid metal. The Th-Cu system was studied in the temperature range of 200° to 700° C. Reaction products are finely divided and well crystallized at temperatures below the melting points. Sodium apparently does not participate as a catalyst in the process, but does promote

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[13] Ruth, J. P. Rare Earth Metals Demand Up for Pipelines in Severe Areas. Am. Metal Market, v. 79, No. 130, July 17, 1972, p. 30.

[14] Baranow, S. The Effect of a Hydrogen Preheat-Treatment on the Oxidation Behavior of Ni-Cr-Al-ThO_2 Alloys. Met. Trans., v. 3, No. 12, December 1972, pp. 3265–3267.

[15] Tomson, J. R. Alloys of Thorium with Certain Transition Metals. VI. The Constitution of Thorium-Nickel Alloys Containing 50%–96% Nickel. J. Less-Common Metals, v. 29, No. 2, October 1972, pp. 183–188.

[16] Childs, B. G., P. J. Harvey, and J. B. Hallett. Optical Absorption Spectroscopy of ThO_2. J. Am. Ceramic Soc., v. 55, No. 11, November 1972, pp. 544–547.

[17] Benz, R. Nitride Layer Growth on Liquid Thorium and Solid Thorium Carbon Alloys. J. Electrochem. Soc., v. 119, No. 11, November 1972, pp. 1596–1602.

[18] Halbfinger, G. P., and M. Kolodney. Activated Sintering of ThO_2 and ThO_2-Y_2O_3 with NiO. J. Am. Ceramic Soc., v. 55, No. 10, pp. 519–524.

[19] Leitnaker, J. M., M. L. Smith, and C. M. Fitzpatrick. Conversion of Uranium Nitrate to Ceramic Grade for Light Water Breeder Reactor: Process Development. Oak Ridge National Laboratory, Metals and Ceramics Division, ORNL-4755, April 1972, p. 54.

the reaction by activating the cooper surfaces.[20]

In connection with the chemical processing of molten-salt breeder reactor (MSBR) fuels, information was sought on mutual solubilities of thorium and certain rare earth lanthanides in bismuth solutions over a temperature range of 350° to 700° C. Although individual solubilities of thorium bismuthides and most lanthanide bismuthides are known, few data are available on their mutual solubilities or the interractions of thorium, bismuth, and the lanthanides. For the study, the system was contained in an argon atmosphere in a molybdenum crucible. The components of the system interracted to form solid compounds.[21]

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[20] Berlin, B. Formation of the Intermediate Phases of the System Thorium-Copper in Liquid Sodium. J. Less-Common Metals, v. 29, No. 4, December 1972, pp. 337–348.

[21] Smith, F. J. Mutual Interaction of Thorium, Lanthanides, and Bismuth in Th-Ln-Bi Solutions: Evidence for Formation of Th-Ln-Bi Compounds. J. Less-Common Metals, v. 29, No. 1, September 1972, pp. 73–79.