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PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters of the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

45. THE ACTINIDES

INTRODUCTION

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THE actinide elements, otherwise known as the *5f* transition series, are the fourteen elements which follow actinium ($Z = 89$) in the Periodic Table. They result from the successive addition of electrons to the empty *5f* orbitals of the precursor element, and are analogous to the lanthanide, *4f*, transition series in this respect. In contrast to the lanthanides, in which the normal oxidation state is +3, both in aqueous solution and in solid compounds, the actinides exhibit a variety of oxidation states in the early part of the series, up to and including americium (Table 1). However, the common oxidation state of americium and the remaining elements in aqueous solution is +3, as in the lanthanides, with the sole exception of nobelium ($Z = 102$), for which the dipositive state appears to be extremely stable with respect to oxidation in aqueous solution, apparently a consequence of the filled *f* shell electron configuration ($5f^{14}$) of the No^{2+} ion.

TABLE 1. KNOWN OXIDATION STATES OF THE FIRST SIX ACTINIDE ELEMENTS*

Th	Pa	U	Np	Pu	Am
		•			2†
	3(?)	3	3	3	*3*
4	4	4	*4*	*4*	4
	5	5	*5*	5	5
		6	6	6	6
			7	7	
				8(?)	

* The common oxidation state (*aqueous solution*) is italicized.
† Isolated in a CaF_2 matrix and more recently as the diiodide.

The stability of the tripositive ions with respect to oxidation or reduction in the latter part of the actinide series is due to thermodynamic factors, as in the lanthanide series. The requirements for such stability in aqueous solution are, first, that the enthalpy of hydration of the tripositive ion should exceed that of the dipositive ion by an amount numerically greater than the value of the third ionization potential and, second, that the enthalpy of hydration of the tetrapositive ion—a somewhat nebulous concept in view of the high charge and polarizing power of such an ion—should exceed that of the tripositive ion by an amount numerically less than the value of the fourth ionization potential[1].

[1] K. W. Bagnall, in *Essays in Chemistry*, Vol. 3, p. 39. Academic Press, Inc., London (1972).

In the earlier part of the actinide series, the high oxidation states which can be attained indicate, at least qualitatively, that the fourth and higher ionization potentials for these elements must be much smaller than those for the corresponding part of the lanthanide series. No experimentally determined ionization potential data are available for the actinides, but the differences between the 4*f* and 5*f* transition series are probably rather similar to those between the 3*d* and 4*d* transition elements. In the case of the 4*d* elements the known ionization potentials are appreciably less than those in the 3*d* series (Table 2) and the radii of ions in the same oxidation state are larger in the 4*d* series than are their counterparts in the 3*d* series. Similarly, the radii of the tripositive actinide ions are about 7% larger than those of the analogous lanthanide ions at the beginning of the actinide series, but this difference in ionic radius decreases with increasing atomic number and the radius of Cf^{3+} is only about 4% greater than that of Dy^{3+} in the lanthanide series. This suggests that the effective nuclear charge to which the 5*f* electrons are exposed is about 14% less than that of the lanthanide analogue at the beginning of the actinide series, falling to 8% less at californium. Since No^{2+} is demonstrably stable to oxidation in aqueous solution, it would seem that for this element the effective nuclear charge may well exceed that experienced by the *f* electrons of ytterbium.

TABLE 2. SOME IONIZATION POTENTIAL DATA FOR 3*d* AND 4*d* TRANSITION ELEMENTS*

Element	Ionization potential (eV)							
	1st	2nd	3rd	4th	5th	6th	7th	8th
Vanadium	6·74	14·65	29·31	48	65·2	128·9	151	174
Niobium	6·77	13·5	28·1	38·3	49·5	103	125	145
Iron	7·90	16·18	30·64	57·1	78	102	128	151
Ruthenium	7·5	16·4	28·6	46·5	63	81	100	119

* Data from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., pp. 797, 910, Interscience Publishers, New York (1966).

The increase in effective nuclear charge with increasing atomic number across the actinide series, as in the lanthanide series, is due to the rather poor screening of one *f* electron by another as the *f* shell fills up. The consequences of this are that the whole *f* shell contracts as the atomic number increases—the lanthanide and actinide contractions—and the fourth, or higher, ionization potentials must also increase across the series, so causing a decline in the stabilities of the higher oxidation states towards reduction.

Much of the work described in this volume relates to two of the earlier actinide elements, thorium and uranium. The main reasons for this apparent imbalance are simply the availability and the ease of working safely with these two elements. Whereas thorium and uranium are readily available by the ton, protactinium (^{231}Pa, a member of the ^{235}U decay chain), neptunium, plutonium and americium are available in gram quantities, but are expensive, and from curium onwards the quantities available decrease steadily from milligram (curium) to submicrogram (fermium, $Z = 100$) amounts and thereafter the availability is measured in atoms. The intensity of the radioactivity per unit mass, or specific activity, increases in the same direction.

Although all the known isotopes of the actinide elements are radioactive, the half-lives of ^{232}Th, ^{235}U and ^{238}U are sufficiently long for them to be found in nature and there are no

major handling problems involved in working with them. This is in marked contrast to the much greater radioactivity hazard arising from the α-activity of protactinium and the synthetic transuranium elements. Because of these hazards, it is necessary to build very expensive laboratories for chemical research on these elements, and the cost involved has restricted fundamental research in this area of the Periodic Table to government supported research establishments, such as Harwell in the U.K., the Argonne and Oak Ridge National Laboratories in the U.S.A. and so on. In establishments such as these the proportion of effort directed to fundamental chemical research is naturally quite small, and a much larger proportion of the research is of an applied nature, directed at the chemistry of reactor systems, particularly to fuel reprocessing and fuel fabrication, and to analytical control. It will be readily apparent from the content of the following sections that much remains to be done in the transuranium, and more particularly in the transplutonium, region of the actinides.

THE ELEMENTS

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1. DISCOVERY

The first of the actinides to be recognized as a new element was uranium detected in a pitchblende specimen from Saxony by M. H. Klaproth in 1789. Berzelius discovered thorium in 1828 and made the first metal preparation by reduction of thorium tetrachloride with potassium, establishing the basic route by which uranium (1861) and the majority of subsequent members of the series have initially been reduced to metal. Actinium was discovered over half a century later in 1899, by Debierne working in the Curie laboratory and independently by Geisel in 1902. The new radioactive species appeared in those processing fractions in which the rare earth elements concentrated and its position as the prototype element of an actinide series corresponding to lanthanum in the rare earth series was early recognized. The metal was not prepared, however, until 1955. Protactinium, the last of the actinide elements occurring naturally in significant quantities (there is 0·34 ppm ^{231}Pa in uranium ores as a decay product of ^{235}U), was discovered by Fajars and Göhring in 1913 in the isotopic form ^{234}Pa; ^{231}Pa was discovered by Hahn and Meitner and independently by Soddy and Cranston three years later.

Although a study of members of the series began almost two centuries ago, the major developments in actinide chemistry have taken place following the discovery of nuclear fission by Hahn and Strassmann[1] in 1939, and the synthesis of neptunium by the irradiation of natural uranium with neutrons, and plutonium by bombardment of uranium with deuterium ions in 1940. The Periodic Table has been extended beyond the actinide series with element 104 (Kurchatovium Ku, Rutherfordium Rf) shown to behave similarly to hafnium[2]. The main sequence of discovery is outlined in Table 1.

Whilst the basis for continuation of fundamental research on these elements, which has entailed the evolution of entirely new experimental techniques to deal on the one hand with the extreme radioactivity and toxicity of these isotopes, and on the other with the small quantities initially available and often short half-lives of the higher isotopes, has been the development of thorium, uranium and plutonium as nuclear fuels, it was not envisaged that higher elements would become technologically significant. There has, however, been a surprising growth of interest in other actinides for new technological developments and over the next few decades Seaborg[3] has predicted that these could become a significant factor in the economics of power production, providing a continuing incentive for further studies.

[1] O. Hahn and F. Strassmann, *Naturwiss.* **27** (1939) 11 and 39.
[2] G. T. Seaborg, J. L. Crandall, P. R. Fields, A. Ghiorso, O. L. Keller and R. A. Penneman, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations (1971), A/Conf. 49/P/841.
[3] G. T. Seaborg, *Nucl. Appl. Technol.* **9** (1970) 830.

TABLE 1

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
89	Actinium	Ac	A. Debierne, *Compt. rend.* **129** (1899) 593 F. O. Geisel, *Ber.* **55** (1902) 3608	^{227}Ac	Uranium ore	Reduction of actinium fluoride with lithium vapour J. G. Stites Jr., M. L. Salutsky and B. D. Stone, *J. Amer. Chem. Soc.* **77** (1955) 237	^{227}Ac
90	Thorium	Th	J. J. Berzelius (1828)		Thorium ore	Reduction of thorium tetrachloride with potassium J. J. Berzelius, *Ann. Physik* **16** (1829) 385	^{232}Th
91	Protactinium	Pa	K. Fajars and O. H. Göhring (1913) O. Hahn and L. Meitner (1917) *Naturwiss.* **6** (1918) 324 F. Soddy and J. A. Cranston, *Proc. Roy. Soc. (London)* **A94** (1918) 384	^{234}Pa ^{231}Pa	Uranium ore concentrates	Bombardment of protactinium oxide with 35 keV electrons in a high vacuum or thermal decomposition of protactinium pentachloride on a hot filament A. V. Grosse and M. Agrass, *J. Amer. Chem. Soc.* **56** (1934) 2200	^{231}Pa
92	Uranium	U	M. H. Klaproth (1789)		Pitchblende	Reduction of tetrachloride with potassium B. Peligot (1841) *Ann. Chim. Phys.* **5** (1842) 7, 42	^{238}U
93	Neptunium	Np	E. McMillan and P. Abelson, *Phys. Rev.* **57** (1940) 1185	^{239}Np	Irradiation of natural uranium with neutrons $^{238}U(n, \gamma) \xrightarrow{\beta^-}$	Reduction of NpF_3 with barium S. Fried and N. Davidson, *J. Amer. Chem. Soc.* **70** (1948) 3539	^{237}Np

TABLE 1 (*cont.*)

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
94	Plutonium	Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy and Al. Wahl (1940) *Phys. Rev.* **69** (1946) 366	^{238}Pu	Bombardment of uranium with deuterium ions $^{238}U(d, 2n)\ ^{\beta^-}\!\rightarrow$		^{244}Pu
95	Americium	Am	G. T. Seaborg, R. A. James, L. O. Morgan, A. Ghiorso (1944/45) *Phys. Rev.* **78** (1950) 472	^{241}Am	Irradiation of plutonium with neutrons $^{239}Pu\ (n, \gamma)\ ^{\beta^-}\!\rightarrow$	E. F. Westman Jr. and L. Eyring, *J. Amer. Chem. Soc.* **73** (1951) 3396 Reduction of trifluoride with barium	^{243}Am
96	Curium	Cm	G. T. Seaborg, R. A. James and A. Ghiorso (1944) Paper 22.2, p. 1554 of *Transuranium Elements*. Nat. Nuclear Energy Ser. Div. IV, Vol. 14B (1949)	^{242}Cm	Bombardment of plutonium with helium ions $^{239}Pu(\alpha, n)$	Barium reduction of trifluoride. J. C. Wolfmann, W. W. T. Crane and B. B. Cunningham, *J. Amer. Chem. Soc.* **73** (1951) 493	^{247}Cm
97	Berkelium	Bk	S. G. Thompson, A. Ghiorso and G. T. Seaborg (1949) *Phys. Rev.* **80** (1950) 781	^{243}Bk	Bombardment of americium with helium ions $^{241}Am\ (\alpha, n)$	Lithium reduction of trifluoride. J. R. Peterson, J. A. Fahey and R. D. Baybarz, Plutonium 1970, *Proc. 4th Internat. Conf.* Pt. 1 (1970) 20	^{247}Bk
98	Californium	Cf	S. G. Thompson, K. Street Jr., A. Ghiorso and G. T. Seaborg (1950) *Phys. Rev.* **80** (1950) 790	^{245}Cf	Bombardment of curium with helium ions $^{242}Cm\ (\alpha, n)$	Lanthanum reduction of oxide and lithium reduction of trifluoride B. B. Cunningham and L. B. Asprey (1971)	^{251}Cf

TABLE 1 (*cont.*)

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
99	Einsteinium	Es	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier and P. R. Fields	^{253}Es	Irradiation of uranium with neutrons in the first thermonuclear explosion		^{254}Es
100	Fermium	Fm	S. H. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizanga, A. Hirsch, W. M. Manning, C. J. Brown, H. L. Smith and R. W. Spence (1952)	^{255}Fm	Ditto		^{257}Fm
101	Mendelevium	Md	A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg, *Phys. Rev.* **98** (1955) 1518	^{256}Md	Bombardment of einsteinium with helium ions ^{253}Es (α, n)		^{258}Md
102	Nobelium	No	A. Ghiorso, T. Sikkeland, J. R. Walton and G. T. Seaborg, *Phys. Rev. Letters*, **1** (1958) 17	^{254}No	Bombardment of curium with carbon ions		^{254}No
103	Lawrencium	Lr	A. Ghiorso, T. Sikkeland, A. E. Larsch and R. M. Latimer, *Phys. Rev. Letters*, **6** (1961) 474	^{257}Lr	Bombardment of californium with boron ions $^{249-252}$Cf + ^{10}B or ^{11}B		^{256}Lr

2. OCCURRENCE, SEPARATION AND PREPARATION OF THE METALS

2.1. Introduction

It is difficult to generalize about the actinide elements under any of these headings. Only two of them, thorium and uranium, occur to any extent in nature, although the former is in fact relatively common. The other elements are made by man via various nuclear transmutation processes, but the scale on which these are carried out, either deliberately or as by-products of some other reaction, varies widely. Plutonium is produced by the ton in reactors in several countries, both for weapons purposes and as nuclear fuel. Neptunium, protactinium and americium are available in gram quantities whilst the other elements are handled in milligram amounts or in the case of the higher actinides built up virtually atom by atom in particle accelerators.

In consequence, of course, the scale of separation techniques also varies widely. Uranium is mined in large quantities for the nuclear power industry and its separation and that of thorium follows fairly normal metallurgical techniques. The purification of these and of the other actinides relies heavily on solvent extraction and ion exchange methods whilst the rarer elements are often separated by chromatographic techniques.

All the actinide elements form very stable compounds, and powerful reducing agents are needed to produce the metal, the action of the alkali or alkaline earth metals on the actinide halides being usually favoured, although the scale of the operation produces wide variations in technique depending on whether the batch is many kilograms of uranium, a few grams of neptunium or a few milligrams of actinium. Electrolysis of aqueous solutions is not feasible because of the reactivity of the metal, but fused salt electrolysis is used for purification of some of the metals. The van Arkel process of thermal dissociation of the iodide has been used to produce gram quantities of very pure thorium and uranium.

The elements are discussed separately in the following sections.

2.2. Actinium

The only isotope of actinium with a half-life long enough ever to permit macroscopic amounts to be studied is ^{227}Ac ($t_{\frac{1}{2}} = ca.$ 22 years) which decays by β^--emission. ^{227}Ac is a member of the decay chain of ^{235}U, but because of its short half-life occurs only in minute quantities in uranium ores (1 ton of pitchblende contains only about 0·15 mg). Furthermore, the presence of rare earths makes the separation difficult. ^{231}Pa decays by α-emission with a half-life of 32,800 years to form ^{227}Ac, but this is also of rather academic interest because of the rarity of protactinium. The only source of milligram quantities of the element is the neutron irradiation of radium:

$$^{226}Ra(n, \gamma)\, ^{227}Ra \xrightarrow[41\ min]{\beta^-} {}^{227}Ac$$

Actinium may then be separated from its daughter products and from the radium by two alternative processes[4,5]. The actinium can be extracted from an aqueous solution of

[4] F. T. Hagemann, *J. Amer. Chem. Soc.* **72** (1950) 768, and *The Chemistry of Actinium*, in *The Actinide Elements*, G. T. Seaborg and J. J. Katz (Eds.), NNES IV, Vol. 14A, p. 14, McGraw-Hill, New York (1954).

[5] S. Peterson, in *The Transuranium Elements*, G. T. Seaborg, J. J. Katz and W. M. Manning (Eds.), NNES II, p. 1393, McGraw-Hill, New York (1949).

controlled pH using a benzene solution of thenoyltrifluoroacetone (TTA), but for separation of cations of different valencies the alternative ion exchange process is a powerful tool. The trivalent actinium and tetravalent thorium are completely absorbed onto Dowex-50 resin from acid solution. The actinium may then be eluted with acid of slightly higher concentration, leaving the thorium still absorbed.

Recently, Baetsle *et al.*[6] have prepared about 18 g of ^{227}Ac as Ac_2O_3 for use as a thermionic power source. Radium carbonate was irradiated to the optimum level, so as to balance production of ^{227}Ac against its conversion to ^{228}Ac and thence to ^{228}Th. The targets were then dissolved in dilute nitric acid and the remaining radium precipitated with 80 % HNO_3, purified and recycled. The thorium and actinium in the filtrate were then separated by anion exchange: the thorium is absorbed from 5 M HNO_3 while the actinium is delayed in the column more than the non-complexing impurity cations. The separated actinium is about 96 % pure.

Only two preparations of metallic actinium have so far been made and in only the second of these was the X-ray pattern of the metal obtained. Stites *et al.*[7] separated the actinium by ion exchange and it was further purified by precipitation as the oxalate which was then ignited to the oxide. The latter was dissolved in hydrochloric acid and the fluoride was precipitated by adding HF. The fluoride was held in a molybdenum microcrucible in a vessel containing excess lithium metal. The latter vaporized on heating by induction in a good vacuum and reduced the fluoride at about 1200°C to form a bead of actinium metal:

$$AcF_3 + 3Li \rightarrow 3LiF + Ac$$

Their three reductions totalled 20 mg. The fluoride was chosen for reduction because it was the easiest halide to prepare in the anhydrous state: lithium was selected as the reductant because the volatility of lithium fluoride drives the reaction to the right.

Because of the small quantities available, the technique used by Farr *et al.*[8] was to carry out the final stages of the preparation of the metal actually in the capillary tube used for the X-ray examination. Actinium oxide was converted to the chloride by reacting the hydroxide with excess ammonium chloride. The powder was transferred to an X-ray capillary on the side of a larger tube. Potassium metal was added to the latter and on heating to 350°C the vapour diffused into the capillary to reduce the chloride. The capillary was then sealed for X-ray examination, with no attempt being made to separate the KCl that was also formed. The metal was contaminated with the hydride and X-ray reflections corresponding to this were also seen. Some doubt must still exist that the four reflections observed were actually due to the metal, although a similar experiment using lanthanum as a stand-in also showed lines of the hydride in addition to those of the metal.

2.3. Thorium[9–12]

The most stable isotope of thorium, ^{232}Th, is an α-emitter with a half-life of $1 \cdot 4 \times 10^{10}$

[6] L. H. Baetsle, M. J. Brabers, P. Dejonghe, A. C. Demildt, A. de Troyer, A. Droissart and M. Poskin, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations (1971) A/Conf.49/P/287.

[7] J. G. Stites, M. L. Salutsky and B. D. Stone, *J. Amer. Chem. Soc.* 77 (1955) 237.

[8] J. D. Farr, A. L. Giorgi, M. G. Bowman and R. K. Money, *J. Inorg. and Nucl. Chem.* 18 (1961) 42.

[9] F. L. Cuthbert, *Thorium Production Technology*, Addison-Wesley, Reading, Mass. (1958).

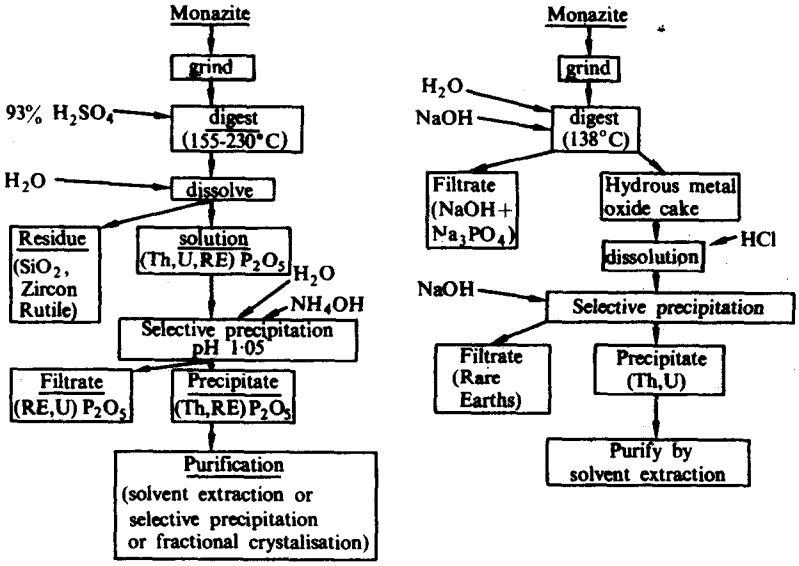
[10] R. G. Bellamy and N. A. Hill, *Extraction and Metallurgy of Uranium, Thorium and Beryllium*, Pergamon Press, Oxford (1963).

[11] N. D. Veigel, E. M. Sherwood and I. E. Campbell, in *The Metal Thorium*, H. A. Wilhelm (Ed.), ASM, Cleveland (1958).

[12] W. L. Silvernail and J. B. McCoy, in *The Encyclopedia of Chemical Technology*, Vol. 20, p. 248, H. F. Mark, J. J. McKetta and D. F. Othmer (Eds.), Interscience, New York (1969).

years, making it handleable without undue precautions. Although thorium is a fairly common element, only a few tons of the element are produced per year, mainly as a by-product of rare earth element production. Thorium is about the 35th most common element, comprising about 0·001–0·002 % of the earth's crust, i.e. it is roughly three times as common as uranium. Whilst the only commercial sources of the material are the monazite sands, there are some rarer minerals containing larger concentrations of thorium. Among these are thorianite, which contains up to 90 % ThO_2 and which has been worked in Madagascar, and thorite, a silicate which contains up to 62 % thorium, which is found in the Western United States and in New Zealand. Monazite is principally a phosphate of the rare earths which contains between 1 and 10 % thoria. It is a constituent of various granites and other igneous rocks, but in too small a concentration to be useful. However, on weathering, its high density means that it is concentrated naturally in the form of sands, notably in Brazil, India and Ceylon, Australia, South Africa and the United States.

After mining, the monazite sands are first concentrated, initially by sluicing to remove the lighter sands and then magnetically which finally produces monazite of about 95 % purity. This is then "opened" by either acidic or basic digestion[9]. These are shown diagrammatically.



ACID OPENING ALKALI OPENING

The separation of thorium from the rare earths after the acid process is accomplished either (a) by dissolving both and adding sodium pyrophosphate to precipitate thorium pyrophosphate, (b) by adding ammonia to decrease the acidity and precipitating the thorium as a basic salt or (c) by using a solvent extraction process with a high molecular weight amine or tributyl phosphate dissolved in kerosene. The thorium is extracted into the organic phase in each case.

The total production (*ca.* 1965) in the Western world is probably about 500 tons per annum of ThO_2.

There are several methods[9] for producing the metal, all being complicated by the high melting point (1750°C). The most used process[13] starts with the oxide which is reduced with calcium. The calcium is granulated, mixed with the powdered oxide and loaded into CaO-lined crucibles. The reaction mixture is heated to 1000°C in an argon atmosphere. Insufficient heat is liberated to melt the thorium.

$$ThO_2 + 2Ca \rightarrow Th + 2CaO\ (-\Delta H_{298} = 9{\cdot}8\ \text{kcal})$$

The reaction mass is then leached with water and dilute acid and the thorium metal recovered as a powder which is pressed and sintered.

If an ingot of the metal is required directly it is possible to reduce thorium tetrafluoride with calcium.

$$ThF_4 + 2Ca \rightarrow 2CaF_2 + Th\ (-\Delta H_{298} = 96{\cdot}4\ \text{kcal})$$

This again does not produce enough heat to melt the thorium, but this can be accomplished by adding sulphur or iodine as a booster. In an alternative method zinc chloride is added, the resulting zinc–thorium alloy being heated subsequently to distill off the zinc. A strong drawback to this process is that the thorium is recovered as a very reactive sponge. This is also true of the method developed by Knighton and Steunenberg[14] in which the thorium oxide or fluoride is mixed with a flux of $MgCl_2$, $CaCl_2$ and CaF_2 and held in contact with a Mg–Zn alloy at about 850°C. The magnesium reduces the thorium compound to the metal which dissolves in the zinc; this process is accelerated by stirring. On cooling, the metal ingot can be easily separated from the flux and the zinc and magnesium are then distilled off as before. This latter method is generally applicable to the earlier actinides, but usually results in material contaminated by oxygen.

An alternative method which also produces a sponge[15] is to reduce the tetrachloride at 900°C with magnesium, having added enough excess magnesium to form a Th 20 w/o Mg alloy. This is molten at temperature and is protected by the $MgCl_2$ and an argon atmosphere. The magnesium is later distilled off under vacuum at 920°C, and the thorium sponge remaining is arc-melted and then purified by repeated electron beam melting—the resulting ingot containing 50 ppm C, 80 ppm O and 35 ppm N.

Ductile high-purity metal has been produced by electrolysis of fused salts[9]. $KThF_5$, $ThCl_4$ and ThF_4 dissolved in mixtures of NaCl and KCl at concentrations of about 10 % have all been tried. The build-up of fluoride ions in the bath was found to decrease the conductivity which eventually stopped the process, so most development has been carried out using the tetrachloride. A bath temperature of about 800°C is usual with a graphite-lined crucible (acting also as the anode) and a molybdenum cathode. Yields are about 90 % and current efficiencies about 75 %. After withdrawing the cathode it is found that an equal weight of salts is entrapped with the thorium. The deposit is chipped from the cathode and crushed and the salts removed by washing with water and dilute sulphuric acid. The washing treatment markedly affects the final product, since any hydrated thorium compounds remaining appear as oxide inclusions in the metal.

[13] G. A. Meyerson, *Proc. Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1955. United Nations, New York, Vol. 8 (1956) P/635, p. 188.

[14] J. B. Knighton and R. K. Steunenberg, USAEC Reports ANL 7057, 7058 and 7059 (1965) and *J. Inorg. and Nucl. Chem.* 27 (1965) 1457.

[15] D. T. Peterson, W. E. Krupp and F. A. Schmidt, *J. Less-Common Metals*, 7 (1964) 288.

Small quantities of very pure metal may be prepared by the van Arkel iodide process[11] in which the non-metallic impurities are removed. Iodine and the impure thorium feed are reacted in a carefully out-gassed vessel to form thorium tetraiodide. This is volatilized at 455–480°C whilst a thorium filament also in the vessel is resistance heated to 900–1700°C. The tetraiodide decomposes:

$$ThI_4 \rightarrow Th + 2I_2$$

depositing the thorium, and the iodine is released to go through the cycle again. The system is not completely self-sustaining and is finally stopped by the formation of some non-volatile lower iodides on the feed material. The product contains about 200 ppm (wt) carbon and less than 100 ppm oxygen and nitrogen.

Scaife and Wylie[16] have used the van Arkel process with a thorium carbide feed. This gave a product containing 40 ppm C, 15 ppm N and 20 ppm O. Considerable purification from metallic impurities was also obtained with the important exception of uranium which was only reduced to one-third of its concentration in the raw material.

Further purification of thorium from interstitial impurities can be obtained by electro-transport[17]. A metal rod is held in an ultra-high vacuum ($\sim 3 \times 10^{-10}$ torr) and heated to 1600°C by a d.c. current of ~ 1900 A/cm^2. The current "sweeps" the impurities to the anode end of the rod, and total impurity contents of better than 50 ppm can be achieved. The same workers also prepared single crystals of α-thorium by cycling the sample a few times through the α/β transformation (1345°C) and then holding the sample for 50 hr just below this temperature.

2.4. Protactinium

There is only a single isotope of protactinium with a half-life over a month, ^{231}Pa, for which $t_{\frac{1}{2}} = 3{\cdot}28 \times 10^4$ years. This is a member of the ^{235}U decay series and protactinium occurs in nature to about the same extent as radium, one ton of uranium containing (at radioactive equilibrium) 340 mg. It is not worth extracting protactinium separately from uranium ores, but fortunately it becomes concentrated in various residues from uranium processing plants. These, of course, differ and so differing methods have been used to extract and purify the protactinium. The earlier ones, which are summarized by Brown and Maddock[18], resulted in the isolation of only a few milligrams of protactinium until the mid-1950s. Maddock and coworkers[19] then studied the distribution of protactinium in the residues from the Springfields (U.K.) uranium plant which was at that time processing a high grade UO_2 ore. They found that much of the protactinium became concentrated in the "ethereal sludge" which separated at the ether extraction stage of the purification. This sludge was retained and 60 tons of it containing over 100 g of protactinium were available. Maddock[19] developed a process for extracting this which was then adapted for larger scale work by Nairn *et al.*[20] who finally produced about 130 g of protactinium. In their method, the sludge was leached with nitric acid and the uranium extracted from the leach liquor with

[16] D. E. Scaife and A. Wylie, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1958, Vol. 4, p. 215.

[17] D. T. Peterson and F. A. Schmidt, *J. Less-Common Metals*, **24** (1971) 223.

[18] D. Brown and A. G. Maddock, *Quarterly Reviews*, Vol. 17, p. 289, Chemical Society, London (1963),

[19] A. Goble, J. Golden, A. G. Maddock and D. T. Toms, *Progress in Nuclear Energy*, Series 3, Vol. II, p. 86, F. R. Bruce, J. M. Fletcher and H. H. Hyman (Eds.), Pergamon, London (1959).

[20] J. S. Nairn, D. A. Collins, H. A. C. McKay and A. G. Maddock, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1958, Vol. 16, p. 216.

tributyl phosphate. $AlCl_3$ was added, the resulting precipitate dissolved in NaOH and the protactinium extracted with di-isobutyl ketone. Final purification was by ion exchange from hydrochloric acid solution.

Several workers have produced the metal. Grosse[21] used two methods. Firstly he bombarded the oxide with 35 keV electrons in a high vacuum: this decomposed the oxide leaving the metal. Secondly, he decomposed the pentahalides on a tungsten filament, i.e. by a van Arkel process. In neither case does he appear to have checked by X-rays that he really had produced protactinium metal, and the former method in particular seems rather improbable. The van Arkel process has surprisingly not been tried by subsequent workers.

Sellers *et al.*[22] reduced 0·1 mg of tetrafluoride with barium vapour at 1400°C in a double beryllia crucible system. The fluoride was placed inside the inner crucible which had a loose fitting cover. The outer crucible contained this and the barium reductant (in large excess). The whole was rapidly heated in a good vacuum with a tantalum spiral. The barium vapour diffused into the inner crucible and reduced the fluoride to several globules of protactinium metal which were identified by X-rays[23].

Four other preparative methods have been used. Marples[24] reduced the tetrafluoride with calcium at 1250°C: the temperature was not sufficient to melt the products and the protactinium metal was present as a powder dispersed in the calcium fluoride slag. Some of the metal was arc-melted into a bead weighing 70 mg, but this was rather wasteful and introduced contamination. The zinc magnesium reductant method due to Knighton and Steunenberg[14] (described above under thorium) also works for protactinium[25], but again the purity of the product is not good.

Cunningham at Berkeley has prepared the metal, also from the tetrafluoride, in two ways. Originally[26] he used a barium vapour reductant in an induction heated tantalum double crucible system, the tetrafluoride being contained in a tungsten wire basket: the metal was formed round the tungsten wires. More recently[27] he has used a barium fluoride crucible, carrying out the reduction at 1300°C. The temperature is then increased to 1600°C when the molten protactinium metal separates as a bead held in contact with the melt by surface tension. This method probably produces the highest purity material.

2.5. Uranium

Uranium is the heaviest element to occur in nature in recoverable amounts, the isotopes, all α-emitters, occurring in the following proportions: ^{238}U, 99·28 %, with a half-life of $4{\cdot}5 \times 10^9$ years; ^{235}U, 0·71 %, half-life $7{\cdot}00 \times 10^8$ years; and ^{234}U, 0·005 %, half-life $2{\cdot}35 \times 10^5$ years.

Whilst care must be taken in handling it (particularly in a dusty form), natural uranium does not require the extreme precautions needed for the other actinides except thorium. Enriched uranium, i.e. uranium containing more of the fissile and more α-active ^{235}U, must be handled more carefully.

[21] A. V. Grosse, *J. Amer. Chem. Soc.* **56** (1934) 2200.
[22] P. A. Sellers, S. Fried, R. E. Elson and W. H. Zachariasen, *J. Amer. Chem. Soc.* **76** (1954) 5935.
[23] W. H. Zachariasen, *Acta Cryst.* **5** (1952) 19.
[24] J. A. C. Marples, *Physico-Chimie du Protactinium*, p. 39, Centre National de le Recherche Scientifique, Paris (1966).
[25] A. Hough and J. A. C. Marples, Unpublished work (1968).
[26] B. B. Cunningham, *Physico-Chimie du Protactinium*, p. 45, C.N.R.S., Paris (1966).
[27] B. B. Cunningham, Private communication to D. Brown (1970).