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Uranium Recovery from Low-Level Aqueous Sources

A. D. Kelmers
H. E. Goeller

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CHEMICAL TECHNOLOGY DIVISION

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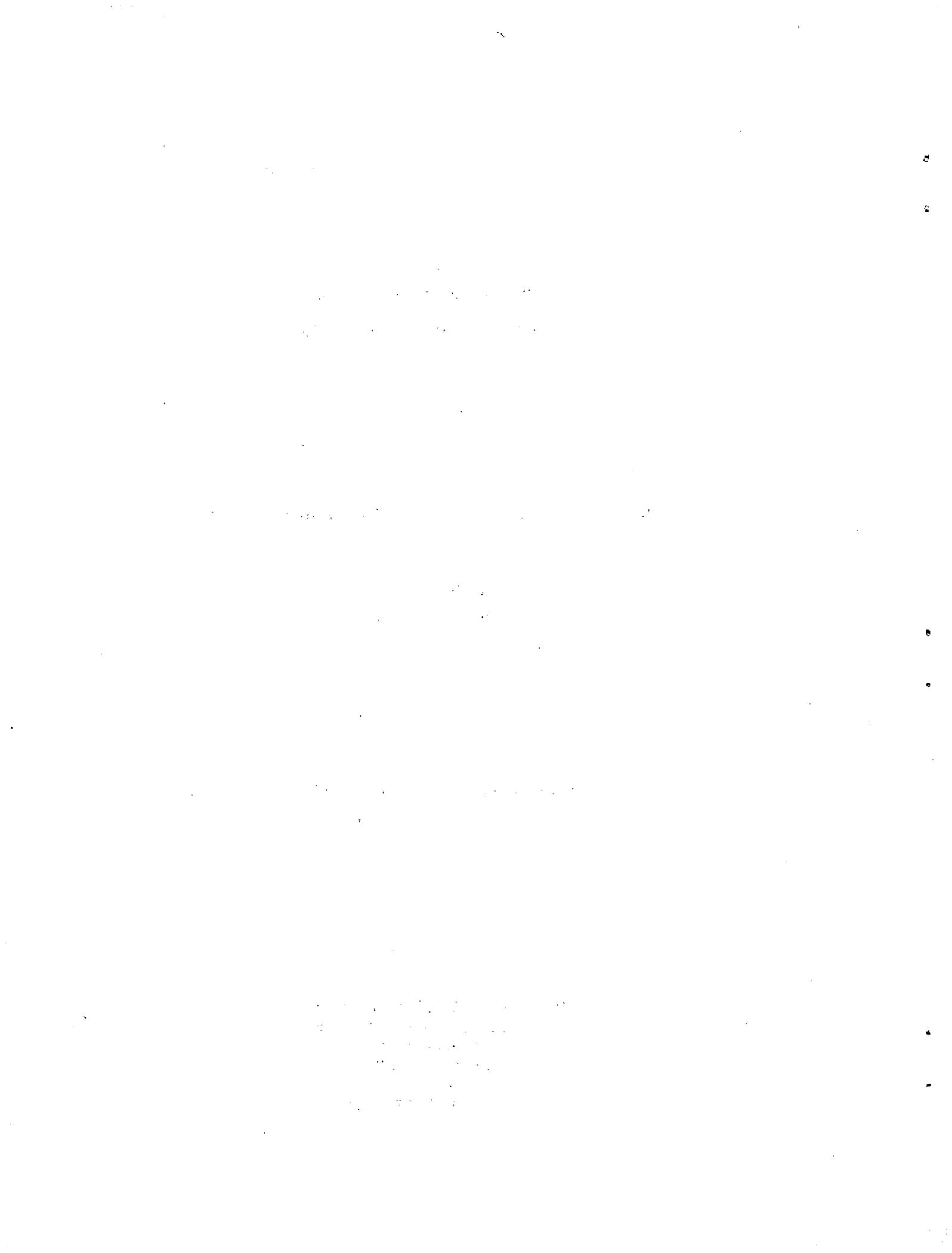
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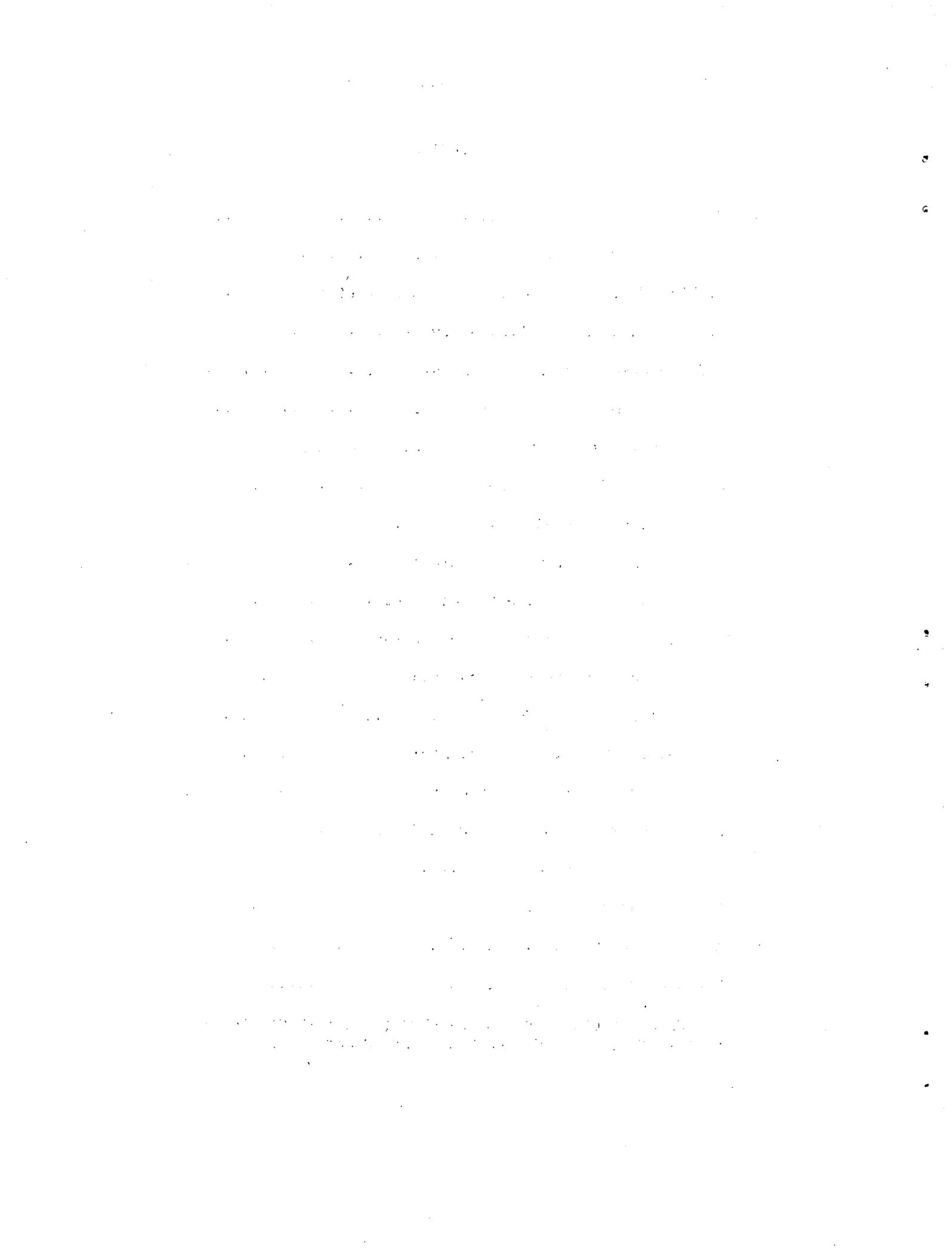


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URANIUM RECOVERY FROM LOW-LEVEL AQUEOUS SOURCES

A. D. Kelmers

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ABSTRACT

The aqueous sources of soluble uranium were surveyed and evaluated in terms of the uranium geochemical cycle in an effort to identify potential unexploited resources. Freshwater sources appeared to be too low in uranium content to merit consideration, while seawater, although very dilute (~ 3.3 ppb), contains $\sim 4 \times 10^9$ metric tons of uranium in all the world's oceans. A literature review of recent publications and patents concerning uranium recovery from seawater was conducted. Considerable experimental work is currently under way in Japan; less is being done in the European countries. An assessment of the current state of technology is presented in this report. Repeated screening programs have identified hydrous titanium oxide as the most promising candidate adsorbent. However, some of its properties such as distribution coefficient, selectivity, loading, and possibly stability appear to render its use inadequate in a practical recovery system. Also, various assessments of the energy efficiency of pumped or tidal power schemes for contacting the sorbent and seawater are in major disagreement. Needed future research and development tasks are discussed. A fundamental sorbent development program to greatly improve sorbent properties would be required to permit practical recovery of uranium from seawater. Major unresolved engineering aspects of such recovery systems are also identified and discussed.

1. INTRODUCTION

This literature review and technology assessment was undertaken to evaluate low-level aqueous sources as potential unconventional uranium resources for the future. Known resources of terrestrial uranium ores are limited and may constrain nuclear power expansion at some future date, depending on the assumed scenario and mix of burner and breeder reactors. Both freshwater and seawater sources of uranium were considered.

Interest in the recovery of uranium from seawater has been heightened by recent news releases^{1,2} which report that the Metal Mining Agency of Japan plans to start a \$10.8 million project to construct a pilot plant that will process 1500 metric tons of seawater per hour and yield 10 kg of uranium each year. By the year 2000, commercial plants will be able to recover 1000 metric tons of uranium per year. Since the previous ORNL assessment³ of the technology for uranium recovery from seawater had not been especially sanguine, an up-to-date reassessment seemed desirable.

A survey of both freshwater and seawater aqueous sources of uranium in terms of the uranium geochemical cycle and inferences concerning the identity of significant potential sources are given in Sect. 2. Section 3 consists of a literature review and assessment of the current state of technology for uranium recovery. Future research and development are identified in Sect. 4.

2. SURVEY OF LOW-LEVEL AQUEOUS SOURCES OF URANIUM

Four billion metric tons of dissolved uranium, at an average concentration of ~ 3.3 ppb,⁴ can be found in the world's oceans. Most of this uranium enters the oceans either from erosion or weathering of uranium-containing minerals on the continents; however, submarine volcanic activity is also responsible for the presence of uranium. A large fraction of the uranium from land-based erosional sources also enters the seas as insoluble uranium in transported sediments, but this uranium is not recoverable since it settles rapidly to the ocean floor. The soluble uranium concentration in the open oceans is fairly constant (directly proportional to salinity), but the amount of soluble uranium (and also uranium in sediments) in streams and rivers varies over about two orders of magnitude (averaging somewhat less than 1 ppb). Man's activities during this century, such as the use of uranium-containing phosphatic fertilizers and the impoundment of uranium ore tailings, have greatly altered the natural conditions.

In this section, the geochemical cycle of uranium is first reviewed in order to provide a guide to the natural locations where higher

concentrations of aqueous uranium sources are more apt to be found. Data are then provided on average uranium concentrations in streams, rivers, and in well water and in stream and subterranean water areas with anomalously high concentrations.

2.1 The Uranium Geochemical Cycle

The mobility of uranium and its occurrence in nature can be explained to a large extent by its geochemical cycle.⁵ A geochemical cycle for any chemical element (or molecular or ionic species) attempts to trace its path in space and time. The description can begin anywhere in the cycle, but the starting point is usually considered to be the time when the generation and intrusion (or extrusion) of magma from a depth in the lithosphere or mantle forms igneous rock. Other major steps in the cycle include weathering and transport (as solution or sediment) to the oceans, precipitation and settling of the element to the seafloor, burial, diagenesis and metamorphism, and finally production of new magma followed by reintrusion to complete the cycle. Each subsequent cycle may differ in some respects from previous cycles.

Ultramafic rocks, which constitute only ~0.25% of all continental rocks, are believed to have the same composition as the earth's mantle — the large reservoir of rock between the earth's crust and the iron-nickel core from which all igneous rocks initially originated. In both ultramafic rocks and the mantle, the uranium concentration is very low, averaging only 0.001 ppm (1 ppb). In all other types of igneous rocks, the average concentration is in the range of ~1 to 5 ppm. Uranium concentration is lowest in basalt (0.9 ppm), which forms the oceanic crust and ~18% of the continental rocks, and highest in granodiorite (2.3 ppm) and granite (4.7 ppm), which are the main igneous rocks in the continental crust. It is also apparent that the much higher concentrations of radioactive uranium (and of thorium and ^{40}K) in crustal rocks result in a much greater heat generation in the crust than in the mantle.

Mechanisms exist that concentrate the uranium in the mantle 1000- to 5000-fold during the production of magma and subsequent intrusion and

solidification of igneous rocks in both oceanic and continental crust. These concentration increases result from only partial melting of mantle rocks in which the minerals with lower melting temperatures (mainly feldspars higher in Na, K, Si, and Al and to a lesser extent calcium) melt, rise toward the surface as lower density magma, and leave behind the unmelted minerals that are richer in iron and magnesium. In this process, uranium strongly tends to follow the molten magma phase.

Magma formation occurs mainly in three tectonic settings. In the first setting, basaltic oceanic crust is formed by the partial melting of mantle rocks below spreading plate boundaries along mid-ocean ridges with intrusion of basaltic magma into the boundary zone. The second setting occurs at plate subduction zones. Here, previously formed oceanic crust plunges slowly back into the mantle beneath either other oceanic crust or an adjacent continental crustal edge. In this process, some of the basaltic oceanic crust, granitic continental crust, and a minor amount of intervening mantle material are partially or completely remelted. The produced magma rises and intrudes the existing rocks in island arcs and new coastal mountains. In this second setting, the uranium concentration is increased up to five times its concentration in basalt. Magma formation is assisted in both settings by the high pressures and/or temperatures due to friction. The third setting involves the passage of tectonic plates over relatively stationary "hot spots" in the mantle, where temperatures are high enough to partially melt the mantle and/or crust. Typical examples are the Hawaiian Islands, the flood basalts of the Columbia River Basin, and the Deccan Plateau in India.

The bulk of the magma in the last two settings can form two diverse igneous rock formations. If solidification occurs well below the surface because of lowered pressures and temperatures, a plutonic body or pluton* is formed; however, if the intrusion is extruded from the surface, large areas are covered by flood basalts, rhyolite flows, or similar volcanic formations. In both cases, the gross composition of the resulting rock is much the same as the magma composition, and most of the uranium from the magma is present in the large formations at low concentrations.

* Includes various types of intrusions such as batholiths (the largest type), stocks, laccoliths, lopoliths, etc.

However, further significant uranium concentration can occur in the last fraction of the magma to solidify since the large ionic radius of uranium makes it difficult for uranium ions to fit into the lattices of the common rock-forming and accessory minerals in the pluton. Because there is some differentiation even in the pluton itself, certain zones such as syenites will be moderately richer in uranium than the original magma. In addition, the lowest-temperature components rich in uranium and other more volatile elements make up the last part of the magma that solidifies. They are most times located in the veins in cracks near the surface of the pluton and in veins, pegmatites, and replacement deposits in the overhead, preexisting country rock. Vein formation in extrusive igneous rocks is much less pronounced because extruded rocks cool and solidify much too rapidly.

Uranium is present in plutons as intermineral-crystal films of uncertain uranium mineralogy, sparsely as uranium accessory minerals (mainly uraninite, UO_2), and as other uranium-containing accessory minerals rich in refractory elements, particularly rare earths, Th, Ti, Nb, and Zr. In veins and pegmatites, uranium occurs mainly as uraninite (UO_2), coffinite [$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$], in mixed uranium-thorium minerals since the two elements are isomorphous, and as the accessory minerals (U, Th, Ti, Fe, and/or rare earths) brannerite and davidite. Sulfide minerals of Fe, Cu, Pb, Zn, Mo, and Co are frequently found in uranium-rich veins. In extrusive igneous rocks (both lavas and pyroclastics), cooling is so rapid that grain formation is generally microscopic or absent (glasslike obsidian), and the uranium is highly dispersed at low concentrations.

In igneous rock formation, uranium is almost always present in the water-insoluble tetravalent state. Prior to the development of a significant oxygen concentration in the earth's atmosphere at the onset of plant photosynthesis 1.5 to 2.0 billion years ago, weathered uranium-containing minerals could not be oxidized to a water-soluble hexavalent form and hence remained in rock detritus. When such detritus was concentrated by fluvial processes, placer-type deposits were produced in much the same way thorium-containing placers are formed today. The quartz-pebble-conglomerate uranium deposits of South Africa and Canada,

which have been protected from oxidation by overburden since Precambrian times, are typical examples of uranium placer deposits of ancient age.

Once the atmosphere achieved its present oxygen content, it became possible to oxidize some exposed uranium minerals to the water-soluble hexavalent form. This is particularly true for the intergranular uranium-rich films in plutons and the uraninite and coffinite in uranium ore veins and pegmatites. Dissolution is still much more difficult, however, for the refractory accessory oxide and silicate minerals also containing rare earths, Th, Ti, Nb, Zr, and U that are still forming placer deposits today.

Solubilized uranium is believed to exist principally as the uranyl carbonate ion $\text{UO}_2(\text{CO}_3)_3^{4-}$. Unless it is reduced back to tetravalent uranium, it is carried rapidly by streams and rivers to the oceans. Insoluble uranium in stream and river sediments also reaches the oceans, but at a much slower rate.

Soluble uranium in underground water travels much slower than that in streams. If the soluble uranium encounters a chemically reducing sediment zone (reductants include inorganic H_2S , SO_3^{2-} , carbonaceous material, and H_2S produced by anaerobic bacteria), it is precipitated, generally as uraninite (UO_2), or adsorbed on the organic materials. In the presence of other soluble elements, new secondary minerals not found in igneous rocks can be formed if these other elements can also be reduced to insoluble forms under the same reducing conditions. Iron is universally coprecipitated (as pyrite), as are Cu, Mo, Se, and Cr; vanadium is frequently also coprecipitated. The most common minerals of this type are carnotite ($\text{K}_2\text{O} \cdot 2\text{U}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$) and tyuyamunite ($\text{CaO} \cdot \text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$). This process leads to formation of the peneconcordant sandstone uranium deposits, the main domestic uranium ore. It also leads to lesser amounts of uraniferous lignite deposits (North Dakota) and deposits in limestone depressions filled with phosphatic, carbonaceous materials (Central African Republic). Considerable soluble uranium is also absorbed on clay minerals and carbonaceous materials.

Soluble uranium that reaches the oceans has an average residence time in solution of $\sim 500,000$ yr.⁶ Insoluble uranium in sediments falls

rather rapidly onto the ocean floor on the continental shelf and is slowly moved to the continental slopes by turbidity currents. Soluble uranium is slowly precipitated by various organic and inorganic processes involving reducing conditions. Once precipitated, the uranium falls to the seafloor to join the insoluble uranium-containing sediments that have already been deposited. Uranium is unusually concentrated in phosphatic sediments derived mainly from the skeletons of marine species that take up some uranium (as a substitute for calcium) while alive and in carbonaceous muds that reduce soluble uranium at or below the seafloor. Much less uranium is present in limestone and carbonaceous-lean red clays which take up only small amounts of uranium.⁴

Carbonaceous marine shales formed from seafloor muds can contain up to 300 ppm uranium (Sweden) but generally contain only 4 to 100 ppm. Phosphate deposits throughout the world contain ~60 to 120 ppm uranium.⁵ Seafloor deposits are sometimes lifted above sea level by vertical earth movements or by changes in sea level during glacial periods. The former method led to the exposure of uraniferous phosphate deposits in Florida and the latter to exposure of material laid down in shallow, inland continental seas. Exposure by the latter process may also be followed by uplift (e.g., the western phosphate deposits).

Sedimentary deposits on continental shelves (miogeosynclines) and continental slopes (eugeosynclines) derived by erosion of island arc and continental margin mountain ranges can become very thick (>10 km). The great pressures involved convert clay muds to shale, sands to sandstone, etc., through diagenesis. When geosynclines become involved in subduction zone processes, the entire geosyncline is foreshortened and thickened. The greatest pressure is exerted on the outer eugeosyncline and lesser pressure on the miogeosyncline. As a result, the former eugeosyncline is highly contorted, and the sedimentary rocks are metamorphosed to schists and gneisses (from shale), marble (from limestone), and quartzite (from sandstone); in this process, the eugeosyncline is converted to new metamorphic basement and added as a new rim to the continental crust (e.g., the eastern U.S. Piedmont zone is the remnants of a coastal mountain range of which only the Blue Ridge remains). New minerals with

higher density are formed (e.g., garnet) during the conversion of sedimentary rock to metamorphic rock. The gross chemical composition of the rock remains the same, but significant changes may occur in the composition of individual minerals. Thus, uranium may change mineral form and composition, but the concentration stays constant.

Because of the great pressures and temperatures involved in the collapse of a eugeosyncline, partial melting of rock takes place and forms new magma. New intrusions and extrusions of igneous rock are then produced, which ends the geochemical cycle. As noted above, collapse of the miogeosyncline is much less violent and results in fold mountains atop the basement complex formed during an earlier subduction event. The gross composition of rocks found in the fold mountains (e.g., the Appalachians) is almost identical to rocks of the former continental shelf.

In addition to the erosion and dissolution of uranium from igneous rocks, much greater weathering and erosion of sedimentary and metamorphic rocks occur worldwide because these types of rock are found in greatest abundance at or near the earth's surface. Of these, shale is the most predominant (~80% of all sedimentary rock) and the most easily weathered.

Release of soluble uranium from shale will depend to a large extent on how tightly uranium ions are adsorbed on the clay minerals. Except under highly oxidizing conditions, little release seems likely, and uranium in shales can be expected to be carried to the ocean mainly as undissolved sediments. The same situation seems to be true for metamorphic shists and gneisses, the main metamorphic rocks.

Although volcanic tuffs (ash) are of igneous origin, they have many of the characteristics of sedimentary rocks. They weather readily because of their large surface area and because fast cooling and solidification have left much residual strain in the particles. Uranium contained in tuffs cannot be adsorbed as readily as that in shales and is easily solubilized, as witnessed by the fact that some uranium deposits found in peneconcordant sandstone were derived from uranium contained in weathered tuff. Fast-cooled lavas exist as volcanic glass (obsidian). Since they are unstable, with respect to a more ordered crystalline state, they also weather rapidly with significant release of soluble uranium.

Finally since limestones and sandstones are less abundant and contain much lower concentrations of uranium (2.2 and 1.7 ppm average) than shale, they are of only minor consequence as sources of soluble uranium. However, sandstones containing significant amounts of organic materials which, as noted above, reduce uranium(VI) to produce peneconcordant deposits are an exception.

2.2 Inferences from Geochemical Cycle

The steps in the geochemical cycle that are important to the present study involve only those situations where uranium is oxidized from insoluble uranium(IV) to soluble uranium(VI). As noted earlier, the most soluble minerals under oxidizing conditions are uraninite and coffinite in veins and pegmatites, secondary uranium minerals in reoxidized sandstone deposits, and most especially, the uranium of unknown mineralogy in intergranular films in granitic plutons and dispersed uranium in volcanic tuffs and obsidian. Adsorbed uranium on shales and uranium in complex accessory minerals rich in rare earths U, Ti, Nb, Zr, and sometimes Th are much less soluble.

As a consequence, the highest naturally occurring uranium concentration in freshwater sources will be derived from weathering of the relatively small areas of uranium-containing veins, pegmatites, and sandstone ore deposits. However, since such sources are small in areal extent, the total uranium contained in local streams also will be small, and concentrations will be lowered rapidly as waters from streams flowing through nonuraniferous areas are combined with the uranium-rich streams.

Since there is a much higher total uranium content (but at lower concentrations) in plutons and volcanic ash deposits of larger areal extent than in the veins, the streams traversing these more extensive areas will have lower, but more uniform, uranium concentrations and, collectively, more total uranium than the richer individual streams in uranium ore locations. Uranium contamination from phosphatic fertilizers in farming regions follows a similar pattern.

Erosion is much more rapid in mountainous regions and in areas with high rainfall. Therefore, more uranium will exist in solution and in

sediments in streams located in areas with either or both of these characteristics. In the eastern United States where rainfall is high and vegetation extensive, weathering is deep and surface concentrations of uranium are low compared to similar geological units in the West where weathering is less extensive.

The remainder of this section seeks to establish average world and U.S. conditions with regard to natural erosion and runoff in order to establish average uranium concentrations and quantities against which "enriched" freshwater sources may be compared.

Only a fraction of the world rainfall results in runoff to the oceans since (1) a great amount of rain falls back directly into the oceans and (2) much of the rain that falls on land is reevaporated back into the atmosphere. The annual residual runoff carried by all rivers to the sea totals $\sim 37 \times 10^{12} \text{ m}^3$ (or metric tons).^{6,7} The amount of water in all rivers⁷ is $\sim 1.165 \times 10^{12} \text{ m}^3$; thus, runoff returns to the sea in an average time of $\sim 12 \text{ d}$; conversely, freshwater is recycled 32 times each year, on the average. Much larger amounts of water are present in freshwater lakes ($125 \times 10^{12} \text{ m}^3$) and subsurface waters on land ($8320 \times 10^{12} \text{ tons}$), but these can be largely ignored since all lake waters and the bulk of subsurface waters reenter rivers on their way to the oceans. Enormous amounts of freshwater are locked up as ice ($30,000 \times 10^{12} \text{ m}^3$), but these too have been neglected. Finally, $\sim 104 \times 10^{12} \text{ m}^3$ of water in saline lakes (e.g., Great Salt Lake) and inland seas (e.g., Caspian Sea) also has been neglected because it is not relevant to this study; however, some of these waters (and their associated brines) may be minor uranium sources.

A second factor that governs the amount of uranium in streams derived through weathering and erosion is the rate of denudation of the land. World data on this subject are sparse and unreliable. However, the USGS has made very careful studies for the United States which indicate that the average rate of domestic land denudation is $\sim 0.061 \text{ mm/yr}$. Based on this value, ~ 1100 million metric tons of rock is transported to the ocean each year. Using this quantity to obtain a world estimate (excluding Antarctica), we find that, very roughly, 21,800 million metric tons of rock is delivered to the oceans annually.

Since the average uranium concentration of all continental rocks is 2.9 ppm, the total uranium entering the seas annually is $\sim 63,200$ metric tons, of which only $\sim 10\%$ is derived from igneous rocks. When this value is divided by the total quantity of water delivered to the sea per year ($37 \times 10^{12} \text{ m}^3$), the average uranium concentration in rivers is 1.7 ppb. However, most of it is in the form of insoluble uranium in sediments. On the average, only 26% of the material in weathered domestic rock is soluble; thus, if this same fractional value applied to uranium, the average concentration of soluble uranium in all rivers is 0.44 ppb, and the total amount of soluble uranium delivered to the oceans, worldwide, is on the order of 16,400 metric tons, of which $\sim 5\%$ or 820 tons is in U.S. rivers.

The average residence time of uranium in the oceans was given earlier as $\sim 500,000$ yr.⁶ Using the data derived above, a residence time of 300,000 yr is obtained (mass of water in the ocean, 1.37×10^{18} metric tons, $\times 3.3 \times 10^{-9}$ uranium per mt/annual delivery of freshwater in rivers, $37 \times 10^{12} \text{ mt} \times 0.44 \times 10^{-9} \text{ mt uranium per m}^3$), which is in fairly good agreement with Bowen's value. Bowen also states that the percentage retention in the ocean is only 0.1% of all uranium in igneous rock ever delivered (uranium in sedimentary and metamorphic rocks is considered to be recycled). This value also agrees fairly well with the above data.

Data on river basin areas, annual runoff, rate of land denudation, and load of dissolved and undissolved materials in the major river systems of the United States are summarized in Table 1;^{7,8} the location and extent of the various basins are given on the map in Fig. 1.⁹ Note in particular that several basins cross international boundaries. This causes some conflict in the data of Table 1, particularly for the St. Lawrence, Western Gulf (mainly Rio Grande), Hudson Bay (mainly Red River of the North), and Pacific Northwest (mainly Columbia River) basins because only basin areas within the United States are used. For the Hudson Bay basin, no problem exists because only headwaters are involved. For the other three, however, there is some contribution to flow from Canada (Columbia and Upper St. Lawrence) or from Mexico (Rio Grande); in the last case, the problem is minor because the Mexican

Table 1. Basin areas, annual runoff, rate of denudation, and annual load in major domestic rivers and river basins

Region	Basin area		Annual runoff		Denudation (cm/10 ³ /yr) ^b	Load Carried by rivers ^b				Major river	
	(10 ³ km ²) ^a	(10 ³ km ²) ^b	(10 ⁹ m ³) ^a	(10 ⁹ m ³) ^b		(cm) ^a	metric tons/ km ² /yr	10 ⁶ metric tons/yr	Percent as solid		Percent as solid
Lower 48 states											
New England	153		92.6		61.0						Connecticut
Hudson-Deleware	80		44.2		53.3						Hudson
Chesapeake	148		70.5		48.3						Susquehanna
North Atlantic	381	383	207.3	188		4.8	126	48	54.9	45.1	
South Atlantic	440		152.1		56.6						
Eastern Gulf	282		136.9		48.3						Mobile
Subtotal	722	736	289.0	291		4.0	110	81	44.3	55.7	
E. Great Lake-											
St. Lawrence	122		55.3		45.7						St. Lawrence
W. Great Lake	210		58.1		27.9						
Total St. Lawrence	332	NG ^c	113.4	NG ^c		NG ^c	NG ^c	NG ^c	NG ^c	NG ^c	
Tennessee-Cumberland	153		81.6		53.3						
Ohio	376		152.1		40.6						
Upper Mississippi	471		85.7		18.3						
Lower Missouri	1186		33.2		2.5						
Lower Missouri	161		31.8		19.8						
Lower Mississippi	166		67.7		40.6						
Upper Arkansas & Red	396		15.2		4.1						
Lower Arkansas & Red	303		109.2		35.6						
Total, Mississippi-											
Missouri	3212	3238	576.5	554	17.9	5.1	132	427	70.9	29.1	Mississippi
Hudson Bay	155	NG ^c	6.4	NG ^c	4.1	NG ^c	NG ^c	NG ^c	NG ^c	NG ^c	Red River of North
Western Gulf	883	829	71.9	42.9	8.1	5.3	142	118	70.9	29.1	Rio Grande
Colorado	668	637	18.0	20.6	2.8	16.5	440	280	94.8	5.2	Colorado
Great Basin	518	NG ^c	13.8	NG ^c	2.8	NG ^c	NG ^c	NG ^c	NG ^c	NG ^c	Humboldt
South Pacific	290	303	88.5	71.5	30.5	9.1	245	74	85.3	14.7	San Joaquin/ Sacramento
Pacific Northwest	666	679	219.8	308	33.0	3.8	101	69	43.4	56.6	Columbia
Total lower 48	7827	5805	1605	1482	20.5	6.1	162	1097	73.8	26.2	
Alaska											
Yukon	513		193		22.6						
Eight Other Major Areas	440		245		55.7						
Subtotal	953		438								
Other	565		NG ^c								
Total Alaska	1518										

^aData obtained from Gerahy et al. *Water Atlas of the United States*, Port Washington, N.Y. 1973.

^bData obtained from J. Gilluly et al. *Principles of Geology*, pp. 70-79, Greeman, San Francisco, 1968.

^cNG - not given.

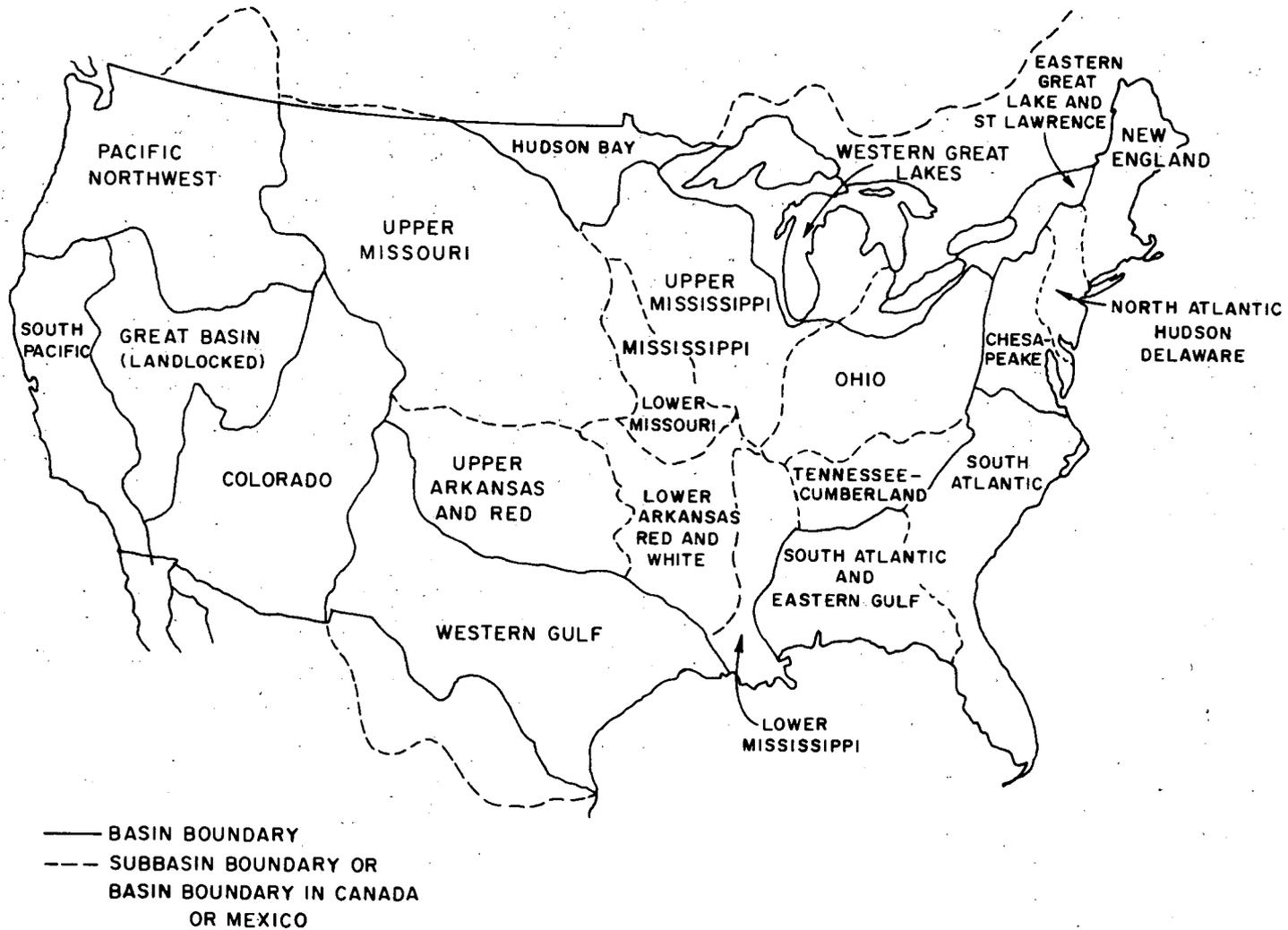


Fig. 1. Location and extent of major U.S. river basins and subbasins (Source: ref. 9).

contribution to flow is very small. Note also that several basins are subdivided by dotted lines (e.g., there are eight subbasins for the Mississippi River basin).

The data in Table 1 show wide variance in parameters. For example, unit runoff varies from 2.8 cm/yr for the arid Colorado basin and the Great Basin to 61 cm/yr for the high-rainfall New England area; the rate of land denudation varies from 4 to 5 cm/10³ yr in the eastern and central United States to 16.5 cm/10³ yr in the Colorado basin; and the fraction of load that is soluble in river water varies from 5% in the Colorado basin to over 50% in the South Atlantic and Eastern Gulf and the Columbia River basins. The Mississippi River, the largest U.S. river and seventh largest in the world,⁸ drains 41% of the area of the lower 48 states and accounts for 36% of the flow in all conterminous rivers.

Man's activities during this century have greatly increased both the rate of land erosion and the amount of uranium available to be delivered to the oceans. Land erosion rates are estimated to have almost doubled in this country, mostly through agricultural activities,⁷ and to have increased by perhaps 30% worldwide.

The extensive use of phosphate fertilizers from which uranium has seldom been removed appears to be the major cause of increased uranium in rivers, particularly in the Mississippi-Missouri system which traverses the main domestic farming area. Annual domestic use of phosphate fertilizer now amounts to 12.4 million metric tons of P₂O₅,¹⁰ which corresponds to ~124 million metric tons of crude phosphate rock (at 10% P₂O₅) containing ~80 ppm uranium. This amounts to ~10,000 metric tons of uranium in phosphate fertilizers that will be added to the soil each year. Of course, the figure will be decreased if there is greater by-product recovery of uranium. It appears that only a small amount is solubilized, so most of the added fertilizer will enter rivers as insoluble sediment as soil erosion proceeds.

Some uranium enters rivers in phosphate-producing areas as a result of the erosion of overburden and tailings piles. The latter source seems to be more important since only 70 to 80% of the P₂O₅ is removed from crude phosphate rock during beneficiation. The other major man-

made source of uranium additions to rivers is in uranium mining areas. Some uranium is available from overburden piles since the leanest ores are not processed. More is available in tailings ponds, as a result of dust being blown off tailing piles or material falling off trucks on haul roads between mines and mills. This is a greater problem in the more populated Gulf Coast mining region. Strict management of such material should preclude release except from the occasional bursting of tailings pond dams. In this event, the bulk of any released uranium should flow to the ocean rather rapidly.

2.3 Uranium in Freshwater Sources

Uranium concentrations have been measured periodically in various rivers by the USGS and by various researchers. More recently, the AEC (now DOE) embarked on the National Uranium Resource Evaluation (NURE) program involving radiometric areal surveys and extensive stream and stream sediment sampling and uranium analysis efforts throughout the United States; numerous water wells were also sampled and analyzed. The accuracy of data taken during many of the earlier studies may be questionable because the analytical techniques used at that time were often inadequate for the very low uranium concentrations encountered. However, great care has been taken by NURE to produce high-quality data, and where results appear suspicious, one or more reanalyses have been conducted.

Data for average soluble uranium concentrations in 11 domestic and 4 foreign rivers and for Lake Superior obtained by Bertine et al.¹¹ around 1970 are summarized in Table 2. The range of concentrations varies from <0.01 to 1.22 $\mu\text{g/L}$ (ppb) and the unweighted average for the 17 values is 0.27 $\mu\text{g/L}$. On a weighted average basis, the average uranium concentration would undoubtedly be much lower because of the low concentrations in the largest rivers — Amazon, Congo, Mississippi, and to a much lesser extent the Rhone, Po, and Susquehanna, all of which are among the world's 50 largest rivers. It is suspected that the analyses, on the average, are low. Only three of the rivers have soluble uranium concentrations above the world average of 0.44 ppb (developed in the

Table 2. Average uranium content ($\mu\text{g/L}$) of several U.S. and foreign rivers^a

River	Sample Location	Uranium concentration ($\mu\text{g/L}$) PPb	Average annual flow ($10^9 \text{ m}^3/\text{yr}$ or km^3)	Rank in flow among world rivers
Domestic				
Klamath	Klamath Glen, Calif.	1.22		
Brazos	Hwy 59, Tex.	1.06		
Colorado ^b	Hwy 59, Tex.	0.35		
Mississippi	Hwy 23, Ak.	0.31	86	
Mississippi	Minneapolis, Minn.	0.10	546	7
Red	Hwy 2, La.	0.10	<50	
Wateree	Hwy 1, S.C.	0.07		
Eel	U.S. Hwy 101, Calif.	0.06		
Mad	Blue Lake, Calif.	0.03		
Russian	Hwy 116, Calif.	0.03		
Lake Superior	Grossport, Ont.	0.02		
Susquehanna	Marietta, Pa.	<0.01		49
Foreign				
Amazon	Santarem, Brazil	0.02	6700	1
Congo	Unknown	0.12	1260	2
Rhone	Pont d'Avignon, France	0.64	53	42
Maipo	Puente Alto, Chile	0.23	45	47

^aData obtained from K. K. Bertine et al., "Uranium Determinations in Deep-Sea Sediments and Natural Waters Using Fission Tracks," *Geochim. Cosmochim. Acta.* 34, 641 (1970).

^bNote that this is not the larger Colorado river that flows to the Gulf of California.

last section). A possible reason for the high value in the Klamath River is that the headwaters drain an area of volcanic ash through a marsh near Carter Lake, Oregon, an extinct volcanic caldera. The uranium content in the Brazos River is high because the river drains extensive agricultural areas near Houston and crosses the uranium-rich Catahoula formation (near the area sampled), which is believed to be the source of uranium in the Gulf Coast ore deposits. The Rhone River in France has headwater streams near French uranium vein deposits. Except for the Colorado River, none of the other rivers pass through any known uraniumiferous areas.

Spaulding¹² reports that the uranium concentration of the Brazos River from 1971 to 1972 at Bryan, Texas, varied from 0.6 to 2.7 ppb, with an average of 1.4 ppb (21 samples); flow during this period ranged from 0.45 to 21.5 billion m³/yr, but a negative correlation between flow and uranium content was observed. USGS measurements on the Red River of the North at Fargo, North Dakota, from 1971 to 1975 (32 samples)¹³ showed a variation from <0.4 to ~4.25 ppb, with an average of 1.35 ppb; flow ranged from 0.2 to 2.2 billion m³/yr. The high values may result largely from the leaching of uranium from phosphatic fertilizers since peak uranium concentrations are observed during the planting and fertilizing season.

Sackett and Cook¹⁴ report a range in uranium concentration in the Mississippi-Missouri River system of from 0.10 to 2.39 ppb. They also state that, on the average, the use of phosphatic fertilizers contributes as much as 0.3 ppb uranium to the runoff.

Nearly all of the sample concentrations reported thus far have been obtained at locations near the mouths of the various rivers. Since the intent of the NURE program was to locate potential uranium ore sources, care was taken to obtain samples that had not been contaminated by man-made activities. To do this, most samples were obtained from small streams and tributaries with drainage basins of ~40 km² or less near their sources. Annual flows from such basins would certainly be very much less than 1 km³/yr. Table 3¹³ gives the location and concentrations of some of the highest uranium content samples taken to date from streams in both the conterminous 48 states and Alaska under the NURE program.

Table 3. Domestic streams with anomalously high uranium content

Number	Location		State and County	Uranium concentration ($\mu\text{g/L}$)	River Basin ^a
	Latitude	Longitude			
1	46.69 N	111.87 W	Montana, Lewis, and Clark	400.7	Mississippi (Missouri)
2	39.58	104.84	Colorado, Arapahoe	147.4	Mississippi (S. Platte)
3	40.34	104.41	Colorado, Adams	142.6	Mississippi (S. Platte)
4	34.98	114.01	Arizona, Mohave	139.2	Colorado
5	28.03	97.45	Texas, San Patricio	61.6	Nueces
6	38.61	99.08	Kansas, Rush	39.3	Mississippi (Kansas)
7	41.61	103.02	Nebraska, Morrill	33.1	Mississippi (N. Platte)
8	28.04	97.44	Texas, San Patricio	29.4	Nueces
9	39.02	101.36	Kansas, Logan	20.4	Mississippi (Kansas)
10	65.39	163.65	Alaska	14.5	Kobuk
11	66.00	159.82	Alaska	9.2	Yukon
12	67.42	158.55	Alaska	8.4	Kobuk

^aDoes not indicate the actual stream from which the sample was obtained.

As shown, only four samples contain over 100 ppb uranium, and only one has a very high 400 ppb uranium. The concentrations of the remaining samples rapidly fall to ~20 ppb or less. The reason for the high value of sample 1 is unknown; samples 2 and 3 may indicate the presence of new uranium vein deposits in the front range of the Rocky Mountains similar to the ones at the Schwartzwalder mine, and samples 5 and 8 are downstream from the Texas sandstone uranium deposits. Most of the stream samples have uranium concentrations that are one order of magnitude greater than concentrations in the larger rivers.

Table 4¹³ gives the highest uranium concentrations in well water from various geological areas in Texas arranged in order of decreasing uranium concentration. In all cases, the analysis was the highest one for a group of closely associated wells from a single aquifer. The number of wells and the mean concentration of the group are also given. In most cases, the mean is only a small fraction of the highest value. As shown, concentrations in the richest wells vary from 42 to nearly 1900 ppb. Samples 1, 3, 4, and 6 are all from the Texas uranium ore district in Webb, Live Oak, and Bee Counties. As noted above, the uranium source for the peneconcordant uranium sandstone deposits is believed to be the uraniferous volcanic ash in the Catahoula formation. Samples 2 and 8 are probably influenced by ash sources in the Texas Panhandle. Sample 12 is possibly affected by eroded and redeposited uranium originally derived from the Catahoula formation. The source of uranium from sample 5 has not been determined.

The remaining samples are from the Big Bend area and have moderate peak and relatively high group analyses. These are influenced by relatively new felsitic volcanics in the Trans-Pecos area that have not been completely devitrified and may still be losing uranium. The sandstones in this area have no suitable reductants to permit formation of peneconcordant deposits. More likely, the uranium will occur in veins of fracture fillings around calderas such as in the Peña Blanca District, Mexico, which is geologically similar to the Big Bend area.

All of the wells reported were generally of low water yield (<10 gpm); they were either low-yield windmill wells (1-5 gpm) or domestic electric stock wells (<10 gpm).

Table 4. Texas well waters with anomalously high uranium content

Number	Location		Quadrangle	Uranium concentration (ppb)	Number of wells in area ^a	Mean uranium concentration of all wells ^a
	Latitude	Longitude				
1	28.17 N	98.60 W	Beeville	1878	173	21.9
2	33.11	101.94	Lubbock	411.3	394	11.0
3	29.06	97.79	Seguin	524	42	0.1
4	29.77	97.68	Seguin	310	71	0.1
5	33.69	97.68	Sherman	298.2	285	0.3
6	29.07	98.70	San Antonio	192.8	60	0.1
7	29.98	103.81	Emory Peak	165.1	55	4.9
8	34.78	100.58	Plainview	106.9	292	7.8
9	34.78	103.79	Emory Peak	104.4	40	7.0
10	29.92	104.06	Presido	89.6	14	6.5
11	29.72	104.06	Presido	60.1	33	7.1
12	29.88	94.05	Houston	43.9	376	0.3

^aThe wells in each group of wells are from the same geologic unit and the same aquifer.

Well samples from the Rocky Mountain area (Wyoming, Colorado, Utah, and Wyoming) are sparse because the water table is far underground and because of the scarcity of wells.

2.4 Uranium Recovery from Freshwater Sources

Although the amount of data provided above is limited, it does show that freshwater is an unlikely source of commercial uranium. When it is realized that at 1 ppb at least 1 km³ of water must be processed to obtain 1 metric ton of uranium, which is only 0.01% of the current annual demand, the difficulties involved will become more apparent. On the other hand, flows from small streams and wells with higher concentrations are too small to be significant. In addition, underground water in the areas of greatest potential is too valuable for agricultural and other uses to be wasted. Flows in large rivers could contribute a significant fraction of needs if entire rivers were processed. However, this seems totally infeasible. Therefore, the remainder of the report will be devoted to a literature review and technology assessment on the recovery of uranium from seawater.

3. URANIUM RECOVERY FROM SEAWATER

The possibility of recovering uranium from seawater has received attention over the past three decades. This interest has arisen from the fact that despite the very low uranium concentration (~ 3.3 ppb¹⁵), the enormous volume of all the earth's oceans contains $\sim 4 \times 10^9$ metric tons of uranium. This uranium, of course, is already in solution, and it has been obvious that if a suitable extractant or sorbent was available, the uranium could, in principle, be readily recovered.

The published information reporting research or describing engineering studies related to uranium recovery from seawater is reviewed in Sect. 3.1. The first work was conducted in Great Britain. Other European countries then became interested, and most recently, an extensive effort has been undertaken in Japan. A comprehensive review of the activities in several foreign countries as of the fall of 1978 is contained in Chapter 15 of ref. 16. An assessment of the current state of the technology is then presented in Sect. 3.2.

3.1 Literature Review

Recently published articles (1977 and later) have been emphasized in this literature review. This review was conducted primarily by searching *Chemical Abstracts*, vols. 86 (1977) through 92 (1980). Much of the earlier work has been well covered in several summary articles and reviews; thus, in compiling this report, no attempt has been made to list all the earlier references. Numerous Japanese patents have recently been issued, and these patents are listed separately in the Appendix.

3.1.1. Recent review articles

Several review articles have appeared since 1977 that summarize the state of development of methods for the recovery of uranium from seawater and include references to much of the earlier work. Three articles have appeared in Japanese journals¹⁷⁻¹⁹ and two in German publications.^{20,21} An extensive bibliography was published in 1979 under DOE funding.^{22,23} These list and discuss essentially all the pertinent work prior to ~1977 to 1978 and preclude the need to perform another independent literature review for the years prior to 1977.

3.1.2. Work in the United Kingdom

The United Kingdom sponsored an active program from the late 1950s to ~1970. This work is described in a recent summary article.²⁴ Screening studies investigated many possible sorbents and identified hydrous titanium oxide (titanic acid) as having the best combination of properties. An engineering analysis of the energy requirements for both tidal basin and pumped schemes was performed. This analysis showed that the energy consumed in pumping seawater through an adsorbent bed could use up a significant fraction of the energy available from the uranium after it is recovered and used in nuclear power plants; thus, design emphasis was placed on a tidal basin concept. It was estimated that a facility to supply 10,000 tons of uranium per year would enclose 777-1034 square kilometers (300-400 square miles) of ocean. Work in the United Kingdom was essentially terminated in the early 1970s when it was calculated that the combined flow of all the water through the Straits

of Dover and the Irish Sea contains <10,000 tons of uranium per year. These findings emphasized the need of siting a recovery plant in or adjacent to a strong ocean current where fresh seawater would be continually supplied and plant effluent removed by the current. Only one recent British publication on the use of hydrated titanium oxide was identified.²⁵

3.1.3. Work in the United States

Little experimental effort has been given to the study of uranium recovery from seawater in the United States. This undoubtedly results from the relatively plentiful uranium resources in the western intermountain region of the United States. Uranium is also recovered as a by-product during phosphoric acid production in this country.

In 1966, the British technology was reviewed at ORNL, and the findings were reissued as a report in 1974.³ This report seriously questioned the very optimistic design parameters employed in the early British cost estimates. By using what were considered to be more realistic values (but still optimistic) for uranium recovery and titanium oxide sorbent losses, much higher cost estimates for uranium recovery were calculated.

Recently, an extensive study of the siting and design of a uranium recovery plant was funded by the DOE Grand Junction Office.^{16,22,23,26} The design work was primarily carried out by Exxon Nuclear and Vitro Engineering, while the site location and oceanographic aspects were covered by Oregon State University. The study concluded that:

1. Uranium is held in solution in the ocean as uranyl carbonate anions.
2. It is held in solution for long periods compared to the circulation and mixing times of the ocean depths.
3. The concentration is ~ 3.3 ppb uranium, equivalent to a total of 4.5×10^9 metric tons; however, only $\sim 0.16 \times 10^9$ metric tons is in the upper 100 meters (the well-mixed surface layer of the oceans) and should be considered accessible for recovery.
4. Freshwater rivers and streams carry too little uranium to be considered practical sources; the entire flow of all the rivers in the world contains only 9000 tons of uranium per year.

5. The only U.S. site with a tidal range favorable to a tidal basin (non-pumped) scheme is Cook Inlet, Alaska. However, the low water temperature of this site would adversely affect the hydrous titanium oxide sorbent properties, and regional circulation patterns of the water would cause considerable back-mixing of plant effluent with influent.
6. A coastal site in Puerto Rico close to the Antilles Current was considered the most favorable site for a pumped seawater plant.
7. The known sorbents for extracting uranium from seawater were compared, and hydrous titanium oxide was identified as the most promising.
8. A chemical process was selected and flowsheet criteria were assumed for a 500-ton U_3O_8 /yr plant.
9. Design and cost estimates were completed for a continuous fluidized-bed recovery facility. The capital costs were \$6.2 billion in 1978 dollars.
10. An annual labor force of 700 was projected for the facility at an annual cost of \$12.5 million.
11. For a plant built by 1995, the cost of extracting uranium from seawater ranged from \$2100 to \$3600 per pound of U_3O_8 , depending on the criteria selected.
12. Key chemical process parameters that had to be estimated due to lack of experimental data included sorbent loading capacity, kinetics, losses due to mechanical attrition and solubility, etc. Since the process is very capital intensive, the costs are very sensitive to the values selected for some of these parameters. Key factors that need further study were identified.

Another DOE-funded engineering evaluation has recently been completed at the Massachusetts Institute of Technology.²⁷ A computer program was developed to simulate engineering performance and provide an economic analysis. A variety of conceptual design systems were considered that employed a hypothetical adsorbent of hydrous titanium oxide coated on particles or on tubes. The equilibrium isotherm and diffusion constant for the uranyl ion-hydrous titanium oxide system were calculated since

they were not experimentally available. The costs obtained were almost one order of magnitude lower than those calculated by Exxon.¹⁶ It was concluded that minimum expected costs of uranium recovered from seawater would be no lower than \$316/lb U₃O₈ in 1979 dollars for state-of-the-art adsorber material. It also was calculated that if the seawater were pumped higher than a 10-ft head, more energy would be consumed in pumping than would be available from the uranium. Research and development objectives to reduce costs were identified.

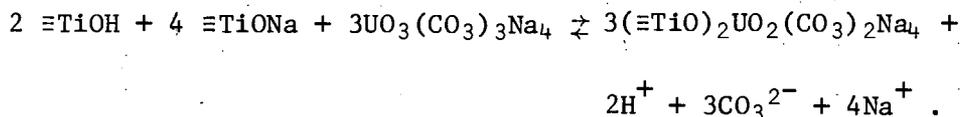
3.1.4. Work in European countries

Based on the number of recent publications, the most active effort in Europe is being carried out in Germany. The present approach has been to consider various adsorbents in an attempt to identify or develop one with suitable properties. Three scoping studies have been published that compare tidal and serial column methods, consider various organic, inorganic, and biological sorbents, and consider the design of a technical installation and the energy balance.²⁸⁻³⁰ Various types of adsorbents other than hydrous titanium oxide are being tested. They include organic ion exchangers,³¹ silica gel,³² brown coal,³³ and cellulose exchangers.^{34, 35} Patents covering these and other sorbents have recently appeared which are based on work done at German installations. The materials covered include magnetic adsorbents,³⁶ silica gel,³⁷ lignite,³⁸ peat,³⁹ micro-organisms,⁴⁰ and special ships to sail about the oceans contacting the adsorber in the ship with the seawater.⁴¹

References to only three recent Soviet Union publications were identified.⁴²⁻⁴⁴ These consider the recovery of uranium from ²³²U-labeled seawater by sorbents such as silica, hydrated iron oxides with collectors such as stearic acid, or ampholytes such as Stearox 6. Coextraction of uranium and copper was considered in one case. In two of these articles, the pH of the seawater was changed by the addition of acid to increase uranium recovery.

A recent French publication⁴⁵ describes the exchange reactions that take place when UO₂(CO₃)₃⁴⁻ is adsorbed by titanium oxide. In this publication, the authors propose that the uranyl moiety is retained on

titanium oxide surrounded by two CO_3^{2-} and two $\equiv\text{TiO}^-$ ligands. The retention equilibrium is given as

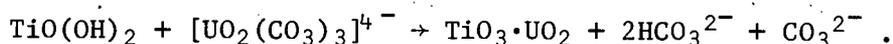


They point out that their findings are not in agreement with earlier British or recent Japanese work.

3.1.5. Work in Japan

Over the last several years, an extensive effort in uranium recovery has been taking place in Japan; this may result from the almost complete absence of domestic conventional uranium resources in Japan. Several research groups have issued a substantial number of papers, and numerous patents have been issued (see Appendix). A wide variety of sorbents are being considered, although much of the work deals with titanium oxide.

Three publications from the Hitachi Research Laboratory⁴⁶⁻⁴⁸ were the first to quantify some important process parameters for the recovery of uranium from seawater with hydrous titanium oxide. The kinetics of adsorption was studied and correlated with surface properties of hydrous titanium oxide crystallites. The mechanism of sorption of the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ion was determined to be



The competitive adsorption of $[\text{UO}_2(\text{OH})_3]^-$ was also considered. The effect of other ions dissolved in seawater was measured and was found to reduce the uranium uptake by a factor of 10. The deposition of calcium carbonate (CaCO_3) from seawater onto the hydrous titanium oxide was primarily responsible for depressing the uranium uptake, although magnesium also was found to have a negative effect.

Another group of investigators at Tohoku University, Department of Nuclear Engineering, has been studying hydrous titanium oxide.⁴⁹⁻⁵² Alternate means of synthesizing the exchanger were tested. Repeated aging and washing were found to be indispensable in obtaining reproducible results and high exchange capacity. The stoichiometry of cation exchange

and acid-base properties of the exchanger were examined. It was concluded that hydrous titanium oxide is a four-functional, weakly acidic cation exchanger. The effects of radiation and heat treatment on the properties of the exchanger were studied, and a structural formula of the exchanger was suggested based on ion-exchange capacity, thermal decomposition curves and x-ray diffraction, and infrared spectra data. It was found that after being allowed to stand in air at room temperature for three to six months, the exchanger showed an abrupt decrease in ion exchange capacity. This was attributed to preferential destruction of the most acidic hydroxyl groups by a dehydration-condensation-type reaction.

Two other groups have been studying composite adsorbents for uranium from seawater, the objective being to combine the favorable properties of several materials into one material. The Government Industrial Research Institute at Takamatsu first studied alumina-activated carbon.⁵³⁻⁵⁶ The properties of the adsorbent and its capacity for uranium recovery from seawater were studied; Freundlich's relationship was observed. Adsorption was temperature and pH dependent. The alumina coating was shown to be bayerite when the adsorbent was prepared at low temperatures and pseudoboehmite at higher temperatures. Heating the adsorbent to 250°C increased the uranium adsorptivity. The group then shifted their attention to zinc-activated carbon composite adsorbent.^{57,58} The product was shown by x-ray diffraction and thermogravimetric techniques to be coated with basic zinc carbonate, $ZnCO_3 \cdot 3Zn(OH)_2 \cdot 2H_2O$, and the composite adsorbent displayed uranium adsorption properties similar to pure basic zinc carbonate. It was found that the strength of the particles increased when the sorbent was granulated with polyvinyl alcohol. In addition, the amount of uranium accumulated was directly proportional to the geometric surface area of the adsorbent granule. Most recently, this research group has been studying titanium-activated carbon.^{59,60} The adsorptivity of seawater constituents was evaluated, and the order was as follows: alkali metals, halogens, and sulfur < boron and alkaline-earth metals < phosphorus and arsenic < transition metals and uranium. Polyvinyl alcohol was tested as a binder. Cyclic adsorption-desorption tests showed that the amount of uranium adsorbed decreased with an increasing number of cycles.

A research group at the Hitachi Research Laboratory has also been studying composite adsorbents, specifically mixtures of titanium(IV)-iron(II) oxides.^{61,62} The composite hydrous oxide was found to be composed mainly of relatively small particles of anatase and large particles of magnetite. Uranium adsorption capacity was related to the mean pore size and the number of surface OH groups. These composite adsorbents are magnetic, and a hydrous oxide adsorbent of 400-625 mesh particle size was magnetically recovered with 99% efficiency after dispersal. The possible application of magnetic separations after contact of the adsorbent with seawater was discussed.

A group at the Okayama College of Science, Department of Chemistry and Nuclear Engineering, has been studying various other extractants. Polyacrylamide gels containing metal hydroxides were investigated,⁶³⁻⁶⁵ and factors affecting the performance of the adsorber were examined. Of the metals tested, only titanium hydroxide was useful for the extraction of uranium from seawater. Absorption performance was not affected by the degree of polyacrylamide cross-linking, but was influenced by any alterations in titanium hydroxide. In other tests, electrolysis with a platinum anode and a stainless steel cathode was used to concentrate the uranium in a $Mg(OH)_2$ precipitate formed at the interface of a seawater-isobutyl alcohol mixture.⁶⁶ The uranium was reported to be completely recovered.

The use of biological systems to recover uranium from seawater is being investigated by a group at Miyazaki Medical College, Department of Chemistry.⁶⁷⁻⁶⁹ The uptake of uranium by various marine microalgae was given as follows: *synechococcus* > *chlamydomonas* >> *chlorella* > *dunaliella* > *platymonas* > *calothrix* > *porphyridium*. Natural polymers such as chitin, chitosan, cellulose, and starch were also evaluated, as was a titanium(IV)-polysaccharide xanthate.

Several other recent papers were noted. In work at Asahi Chemical Industry, it was shown that foam collected at the seashore was ten times more concentrated in uranium than normal seawater, and beach sand was enriched 10 to 100 times over other sand.⁷⁰ The use of chelating resins was investigated at Kumamoto University,⁷¹ and uranium recovery by a polymer-bound macrocyclic hexaketone was tested at Kyoto University.⁷²

The application of the existing technology to the recovery of uranium from seawater was discussed in two recent articles.^{73,74}

3.1.6. Work in other countries

The results of yet another screening program to evaluate adsorbents to scavenge uranium from seawater were reported in an article from India.⁷⁵ Hydrated titanium oxide was again identified as having the best properties — rapid pickup and good recovery. An article from the People's Republic of China on the mechanism of uranium adsorption on titanium hydroxide was also noted.⁷⁶

3.2 Assessment of the Current State of Technology

Despite three decades of effort, the current technology for the recovery of uranium from seawater can only be described as primitive. Much of the effort has gone into empirical experimental screening studies to evaluate possible existing adsorbents or into calculating engineering cost estimates. Little work describing comprehensive process development efforts that would establish firm process parameters has been reported.

Several engineering design and cost estimate studies of uranium recovery from seawater using hydrous titanium oxide have been completed in the last two decades. Since the results of comprehensive process development efforts have not been published and values have not been established for many of the key process parameters, these engineering studies can be no more accurate than the assumed values for the process parameters. Also, a complete process flowsheet has never been reported based on actual tests. It is not surprising then that estimates for the cost of uranium production vary by more than one order of magnitude. Furthermore, estimates of the energy efficiency of uranium recovery show a similar variation. The most recent energy analysis²⁷ states that if the seawater has to be pumped more than 10 ft in height, more energy is consumed in pumping than could be generated by the uranium in a typical LWR, assuming no other energy requirements in the recovery process and

100% uranium recovery. Hence, all published values of costs and energy efficiency probably should be viewed with healthy scepticism.

The concentration of uranium in seawater is at least three orders of magnitude more dilute than that in any commercial process for the economic recovery of any metal. This fact therefore places extreme requirements on the properties of the adsorbent selected for uranium recovery from seawater. The properties of a successful extractant for economic recovery of uranium from seawater can be characterized in general terms, as listed below. The uranium adsorbent is qualitatively compared with the state of development of hydrous titanium oxide. Hydrous titanium oxide was selected for this comparison since screening tests conducted over three decades in several different countries have repeatedly identified it as being the best. A successful extractant must have the following characteristics:

1. Very high distribution coefficient, since uranium is so dilute in seawater. To obtain reasonable adsorbent loading levels, distribution coefficients of 10^6 to 10^8 would be needed. No known extractants for any metal from any solution have distribution coefficients this high. The best practical liquid extractants have demonstrated distribution coefficients of $\sim 10^5$, while distribution coefficients for solid ion exchangers are more typically 10^3 to 10^4 . The value for hydrous titanium oxide for uranium from seawater was given in ref. 48 as 2×10^4 .
2. A very high selectivity, since seawater contains many other ions at much higher concentrations. The adsorption of uranium from seawater on hydrous titanium oxide compared to synthetic uranium solutions is reported to be one order of magnitude less due to calcium carbonate extraction.^{4 8} Thus, loaded hydrous titanium oxide may contain 200 times as much calcium and magnesium as uranium.¹⁸
3. A high loading so that significant quantities of uranium can be recovered on a small volume of sorbent. The reported concentration of uranium on loaded hydrous titanium oxide is only in the range 100 to 1000 ppm due to the combination of the distribution coefficient and selectivity characteristics. Thus, further concentration and

purification steps must be employed after the uranium has been adsorbed onto the hydrous titanium oxide. These additional steps have never been clearly defined experimentally, and no significant samples of purified uranium prepared from seawater have been reported.

4. Rapid loading kinetics in order to minimize contact times. This is very important in a seawater scheme because of the very large volumes of water involved. Recent kinetic data^{4,5} show contact times of 1 to 2 h for hydrous titanium oxide with seawater in order to attain equilibrium. Such long times are highly undesirable and would greatly increase the size of any proposed installation; conversely, shortened contact times would decrease overall recovery efficiency.
5. Rapid elution kinetics. The eluant should ideally be different from the extraction medium so that a second purification step can employ a different technique. Unfortunately, only concentrated carbonate or bicarbonate solutions have proven effective for stripping uranium from hydrous titanium oxide without destroying the adsorbent. Thus, the uranium in the eluate still is very dilute in a concentrated carbonate solution, and a difficult second purification step must be undertaken. This second step has never been defined experimentally. Elution kinetics also are reported to be very slow, and extended contact times were required.^{17,18}
6. Very low losses of the extractant for favorable process economics and to avoid contamination of the ocean. Data on the physical stability of hydrous titanium oxide and losses during contacting due to attrition or solubility are fragmentary but suggest that losses may be very significant economically.³ Furthermore, since uranium is sorbed only on the surface of the particles, any surface loss as dispersed fines also would represent a preferential uranium loss.
7. Low cost, since very large volumes would be required in any recovery scheme to contact the large volumes of seawater. The losses must also be extremely low to minimize costs. Few reported values exist for these aspects of hydrous titanium oxide.

Most hydrous metal oxide precipitates have an indefinite or gel-like structure and are composed of a variety of bonds and cross-linkages. They may have several types of surface oxide and hydroxide groups. Thus, chemical properties such as ion adsorption can vary dramatically, depending on the preparation and history of the sample. Hydrous titanium oxide seems to be no exception. Numerous research groups have reported rather different exchange properties and stabilities for hydrous titanium oxide as well as different equations for the exchange reaction. This undoubtedly results from differences in the preparation and treatment of the samples. This situation complicates attempts to quantitatively compare work by different research groups.

4. NEEDED FUTURE RESEARCH AND DEVELOPMENT

The discussion in this section is limited to uranium recovery from seawater since no significant freshwater sources were identified.

4.1 Chemical Development

Every technological assessment or engineering analysis concerning the recovery of uranium from seawater has identified inadequate adsorbent characteristics as limiting the application of the concept. Research and development to improve the adsorbent has been recommended in many previous reports. Although extensive screening programs carried out over two decades in several countries have repeatedly identified hydrous titanium oxide as the best adsorbent material available, it still falls far short of the necessary adsorbent properties (see Sect. 3.2).

Significant future progress in developing greatly improved adsorbents can probably only be achieved through a long-term fundamental chemistry research program. A multi-year effort involving several people could be required to develop a viable experimental approach. Essentially, significant breakthroughs to new levels of understanding of adsorption and/or ion exchange technology will be required in what is a relatively mature technological area.

The research program should be comprised of the following elements:

1. Information exchange — the literature review (Sect. 3.1) revealed that at least six to ten laboratories, primarily in Japan but also in Germany, have on-going research efforts to develop and apply adsorbents for uranium recovery from seawater. It would be highly desirable to establish an information exchange mechanism with these laboratories.

2. Soluble species identification — additional information is needed to actually identify the uranium species in seawater; $\text{UO}_2(\text{CO}_3)_3^{4-}$ has been assumed to be the form, based on known stability constants.

3. Fundamental sorption studies — The factors controlling anionic adsorption or ion exchange of metal carbonate should be identified and quantified so as to maximize the distribution coefficient rejection of other carbonates and sorption-desorption kinetics. Few metals form soluble carbonate anionic complexes, and only limited existing extraction technology is available to guide this work. Most uranium recovery systems involve acidic systems where uranyl cations, uranyl sulfate, or nitrate complexes are extracted or adsorbed; thus, these experiences are not applicable to seawater recovery systems. Carbonate leaching of some uranium ores followed by anion exchange has been employed. Work of this nature would offer guidance for the development of advanced sorbents.

4. New sorbent development — Using the fundamental information acquired, sorbents for uranium from seawater should be prepared in developmental quantities and evaluated in experiments at an ocean facility so that practical aspects such as fouling due to marine growth or mineral deposition can be evaluated as well as sorption properties.

4.2 Engineering Studies

Obviously, unless the recovery plant can deliver a substantial energy gain, the entire concept of uranium recovery from seawater is invalid. A critical analysis of the energy efficiency of uranium recovery from seawater should be carried out. Previous estimates have shown a wide variation. Since most of the energy is involved in handling the truly enormous volume of seawater associated with any practical-sized recovery plant, such an analysis could probably be made initially

using a generically defined sorbent candidate. The results of some previously published analyses have seemed to preclude pumped schemes because of the pumping power required. Other studies have eliminated tidal basin schemes due to the lack of suitable sites and ecological disturbances as well as the size of civil works involved. The results of such energy efficiency analysis could be used to help establish minimum adsorbent criteria for the adsorbent development work. It has been estimated²⁷ that a conventional LWR reactor requires an annual replacement of 200 tons of uranium. Thus, a 10,000-metric ton/yr uranium-from-seawater plant would refuel 50 LWRs annually. At 100% uranium recovery efficiency, an ocean stream equivalent to 25 times the annual Mississippi River flow would have to be processed to recover 10,000 metric tons/yr. This scale of operation raises certain fundamental engineering questions: Can a flow of this magnitude be pumped through adsorbent beds and returned to the sea in a manner such that no back-mixing with plant influent occurs and still achieve an attractive overall positive energy balance? Can any sort of non-pumped (tidal flow, etc.) scheme offer a more attractive energy balance after consideration of the civil engineering works necessary to confine this non-pumped flow? A generic engineering examination of these and related questions could offer considerable guidance to considering the practical aspects of uranium recovery from seawater.

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7. APPENDIX:

RECENT JAPANESE PATENTS (KOKAI) SPECIFICALLY PERTAINING TO
URANIUM RECOVERY FROM SEAWATER

These patent references were located by searching *Chemical Abstracts*, Vols. 86 (1977) through 92 (1980). The titles, patent numbers, and a brief description are given along with the *Chemical Abstracts* reference number. They are listed chronologically by patent number.

Fibrous Adsorbent, Kokai 76-99,696; polymer containing arsonic acid and substituted aromatic acid; Chem. Abstr. 87, 28,830 (1977).

Recovery of Uranium from Sea Water, Kokai 76-149,815; assemblies of adsorber in a bank or net is moved countercurrently in seawater; Chem. Abstr. 86, 143,563 (1977).

Collection of Uranium from Sea Water, Kokai 76-151,614; absorber chains are hung with a rope from rafts; Chem. Abstr. 86, 143,588 (1977).

Uranium from Sea Water, Kokai 77-9,614; absorber units are hung from a raft and positioned by at least one buoy; Chem. Abstr. 86, 143,571 (1977).

Uranium Adsorption from Sea Water, Kokai 77-29,479; porous polyvinyl acetate sheet is impregnated with titanitic acid; Chem. Abstr. 87, 71,467 (1977).

Heavy-Metal Adsorbent, Kokai 77-29,480; fine pore material is treated with titanitic acid; Chem. Abstr. 87, 70,377 (1977).

Uranium Adsorbents, Kokai 77-29,489; sorbents consist of hydrolyzate of titanium tetrachloride on a solid support composed of oxides, sulfates, phosphates, or silicates; Chem. Abstr. 87, 71,468 (1977).

Uranium Adsorbent, Kokai 77-28,490; adsorbent consists of crushed mixture of inorganic support and titanium compound; Chem. Abstr. 87, 71,469 (1977).

Heavy-Metal Ion Adsorbent, Kokai 77-28,593; resin is obtained by condensation of aromatic carbonyl compound and carboxylic acid hydrazide; Chem. Abstr. 87, 73,023 (1977).

Heavy-Metal Adsorbing Agent, Kokai 77-29,890; quinaldic acid derivative and formaldehyde are polymerized to form adsorbent; Chem. Abstr. 87, 104,929 (1977).

Uranium from Sea Water, Kokai 77-37,506; adsorbers are floated on seawater surrounded by a fence; Chem. Abstr. 87, 9234 (1977).

Separation of Uranium, Kokai 77-104,408; uranium is adsorbed on cement; Chem. Abstr. 88, 10,259 (1978).

Uranium Compound Adsorbent, Kokai 77-114,486; cotton dissolved in concentrated phosphoric acid and titanium tetrachloride is added to form precipitate; Chem. Abstr. 88, 77,168 (1978).

Uranium Collector, Kokai 77-114,510; absorbent is composed of phenol-formaldehyde resin containing phosphoric acid groups; Chem. Abstr. 88, 10,274 (1978).

Uranium Collector, Kokai 77-114,511; a cation exchange resin is coated with hydroxides or carbonates of metals; Chem. Abstr. 88, 10,275 (1978).

Porous Adsorbent for Uranium Compound Adsorption, Kokai 77-114,580; vinyl monomer contains hydrophilic groups cross-linked to another vinyl monomer; Chem. Abstr. 88, 77,167 (1978).

Uranium Adsorbents, Kokai 77-114,586; fibrous product is formed by contacting a polymer adsorbent solvent and a coagulating solution at high shear; Chem. Abstr. 88, 124,499 (1978).

Uranium Adsorbents, Kokai 77-114,587; titanitic acid is bonded to inorganic porous material; Chem. Abstr. 88, 124,500 (1978).

Uranium Adsorbents, Kokai 77-114,588; swelling polymer is saturated with titanitic acid solution and then neutralized; Chem. Abstr. 88, 124,501 (1978).

Collection of Uranium in Sea Water, Kokai 77-135,814. Foam on seawater is suctioned and collected. Foam is reported to be ten times more concentrated in uranium than bulk seawater. Chem. Abstr. 88, 64,623 (1978).

Heavy-Metal Ion Adsorbent, Kokai 77-156,793; titanitic acid hydrosol on porous polyvinyl alcohol or activated carbon was used; Chem. Abstr. 88, 123,259 (1978).

Uranium Collection from Sea Water by Adsorption, Kokai 78-5,090; uranium is adsorbed on a magnetic adsorbent consisting of spheres of magnetic iron oxide core and titanitic acid adsorbate exterior; Chem. Abstr. 89, 92,027 (1978).

Heavy-Metal Adsorbents, Kokai 78-5,091; a porous substrate impregnated with titanitic acid is used; Chem. Abstr. 89, 93,026 (1978).

Heavy-Metal Adsorbents, Kokai 78-23,889; adsorbent is prepared by coupling diazotized aminostyrene copolymers; Chem. Abstr. 89, 114,559 (1978).

Heavy-Metal Adsorbent, Kokai 78-23,890; a polyaminostyrene copolymer is diazotized and then coupled with benzamide; Chem. Abstr. 89, 114,560 (1978).

Heavy-Metal Adsorbents, Kokai 78-23,891; a polyaminostyrene copolymer is diazotized and coupled with a catechol derivative; Chem. Abstr. 89, 93,062 (1978).

Heavy-Metal Adsorbents, Kokai 78-27,690; chloromethylated or chlorosulfonated styrene copolymers are treated with benzamide; Chem. Abstr. 89, 203,971 (1978).

Heavy-Metal Adsorbents, Kokai 78-27,692; adsorbent is prepared by polycondensation of benzoic acid amide derivatives with formaldehyde; Chem. Abstr. 89, 203,970 (1978).

Heavy-Metal Adsorbents, Kokai, 78-28,690; a chloromethylated or chlorosulfonated polystyrene is reacted with a catechol derivative; Chem. Abstr. 89, 114,566 (1978).

Heavy-Metal Adsorbents, Kokai 78-29,393; adsorbent is prepared by polycondensation of 4-hydroxybenzimidazole or derivatives with formaldehyde; Chem. Abstr. 89, 203,957 (1978).

Uranium Adsorbents, Kokai 78-63,289; a metal hydroxide is adsorbed on porous activated carbon beads prepared by carbonization of porous spherical organic polymers; Chem. Abstr. 90, 26,854 (1979).

Uranium Adsorbents, Kokai 78-104,586; micropowdered titanitic acid, galena, basic zinc carbonate, and an organic binder are extruded to form a column; Chem. Abstr. 89, 201,049 (1978).

Uranium Extraction from Sea Water, Kokai 78-115,601; magnetic adsorbent is contacted with seawater; Chem. Abstr. 90, 58,758 (1979).

Chelating Resins and Fibers for Recovery of Uranium from Sea Water, Kokai 78-126,088; resins with nitrite groups are treated with hydroxylamine; Chem. Abstr. 90, 88,278 (1979).

Uranium Leaching from Seashore Sand, Kokai 79-28,702; sand is leached with hydrochloric acid; Chem. Abstr. 91, 77,264 (1979).

Magnetic Composite Uranium Adsorbent, Kokai 79-42,387; titanium sulfate is precipitated on magnetite or ferrite particles, and the adsorbent is magnetically separated from seawater; Chem. Abstr. 91, 77,376 (1979).

Recovery of Uranium in Sea Water, Kokai 79-61,018; titanitic acid is used in foam flotation of uranium from seawater; Chem. Abstr. 91, 77,392 (1979).

Concentration of Uranium in Water by Selective Adsorption, Kokai 79-67,509; cation exchange or chelate resin loaded with iron or titanium is used; Chem. Abstr. 91, 94,866 (1979).

Recovery of Uranium in Sea Water, Kokai 79-79,111; calcium and/or carbonate ions are first removed from seawater, and then uranium is adsorbed on hydrated titanium oxide; Chem. Abstr. 91, 126,680 (1979).

Concentration of Uranium, Kokai 79-87,622; filaments having quaternary ammonium and/or pyridyl-type ion exchange groups are used; Chem. Abstr. 91, 196,748 (1979).

Utilization of Sea Water as Uranium Source, Kokai 79-107,819; adsorbents are added to the reservoir of a power plant and filtered out during discharge of reservoir; Chem. Abstr. 92, 97,329 (1980).

Titanic Acid System Uranium Adsorbent, Kokai 79-119,314; titanium and iron solutions are hydrolyzed to form a pelletized adsorbent; Chem. Abstr. 92, 43,899 (1980).

Regeneration of Uranium Adsorbent, Kokai 79-124,883; deteriorated titanic acid adsorbent is treated with hydrochloric acid and then ammonium compound to remove calcium and magnesium compounds; Chem. Abstr. 92, 62,460 (1980).

Titanic Acid as Uranium Adsorbent, Kokai 79-124,900; titanium solution in the presence or absence of iron is neutralized to form as adsorbent; Chem. Abstr. 92, 96,263 (1980).

Recovery of Uranium from Sea Water, Kokai 79-125,112; powdered hydrated titanium oxide magnetic adsorbent is packed into tubes; Chem. Abstr. 92, 114,188 (1980).

Magnetic Uranium Adsorbent, Kokai 79-128,994; an iron salt and an aluminum salt were neutralized to form an adsorbent; Chem. Abstr. 92, 47,810 (1980).

Composite Adsorbent for Recovery of Uranium from Sea Water, Kokai 79-133,487; activated carbon is mixed with alkaline-earth phosphate; Chem. Abstr. 92, 114,194 (1980).

Recovery of Uranium Adsorbent in Sea Water, Kokai 79-135,686; co-precipitated adsorbent is separated magnetically; Chem. Abstr. 92, 62,475 (1980).

Collection of Uranium in Sea Water in an Electric Plant, Kokai 79-137,415; magnetic adsorbent is added to reservoir and collected magnetically; Chem. Abstr. 92, 114,202 (1980).

Collection of Uranium in Sea Water by Tide Level, Kokai 79-137,414; magnetic adsorbent is contacted at lock gate of reservoir and is collected magnetically; Chem. Abstr. 92, 114,203 (1980).

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