CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

REPORT 79-21

REMOVAL OF RADIONUCLIDES FROM PROCESS STREAMS — A SURVEY

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

Energy, Mines and
Resources Canada

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REMOVAL OF RADIONUCLIDES FROM PROCESS STREAMS - A REVIEW

by

I.J. Itzkovitch* and G.M. Ritcey**

CANMET REPORT 79-21

MINERALS RESEARCH PROGRAM

MINERAL SCIENCES LABORATORIES

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* Head, Hydrometallurgy, Ontario Research Foundation

**Head, Extraction Metallurgy, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

FOREWORD

The Canada Centre for Mineral and Energy Technology (CANMET) of the federal department of Energy, Mines and Resources Canada has been involved in a major research effort devoted to treating uranium bearing ores by both conventional and novel technologies. This program is being carried out with the objective of increasing the recovery of uranium while conforming to environmental guidelines of federal and provincial agencies. All effluents from uranium plants must therefore contain acceptably low levels of metals, salts and radionuclides.

CANMET, through the federal department of Supply and Services, commissioned the Ontario Research Foundation to assess techniques for removing the radionuclides radium 226, lead 210 and thorium 230 from sulphate, carbonate, nitrate and chloride process streams. The sulphate and carbonate streams are produced by conventional processing under investigation at CANMET for treating low-grade complex ores.

Program objectives were to:

1. Assess critically the literature on isolation and chemical-analytical methods for removal of radionuclides for chloride, sulphate, nitrate and carbonate liquors.
2. Review basic chemistry of the radionuclides of Ra^{226}, Th^{230} and Pb^{210}.
3. Prepare a summary of capital and operating costs for radionuclide disposal or isolation by selected processes.
4. Determine the best practical technology and the chances for technical success for implementing the isolation and disposal routes for minimizing radionuclide levels for existing as well as non-conventional processes.
5. Propose a research plan for bench-scale evaluation of alternative isolation and disposal methods.

The contract was performed by the first author, I.J. Itzkovitch of the Process Metallurgy Division, Department of Metallurgy, Ontario Research Foundation. G.M. Ritcey, of the Ore Processing Laboratory, Mineral Sciences Laboratories of CANMET, who is the second author, was the Scientific Authority for contract 22SQ-23440-7-9116 with Ontario

Research Foundation. In the interests of producing a document for public distribution in the shortest time possible, the original report as prepared by the contractor has been reproduced in the form submitted.

D.A. Reeve
Director
Energy Research Program

AVANT-PROPOS

Le Centre canadien de la technologie des minéraux et de l'énergie du ministère fédéral de l'Energie, des Mines et des Ressources Canada est impliqué dans une recherche importante portant sur le traitement des minerais porteurs d'uranium en employant les technologies classiques et nouvelles. Ce programme a comme objectif d'augmenter la récupération de l'uranium tout en se conformant aux normes des agences fédérales et provinciales sur l'environnement. Tous les effluents provenant d'usine d'uranium doit donc contenir un niveau acceptable de métaux, de sels et de radionucléides.

Le CANMET, par l'entremise du ministère fédéral des Approvisonnements et Services, ont retenu l'Ontario Research Foundation afin d'évaluer les techniques pour l'enlèvement des radionucléides radium 226, plomb 210 et thorium 230 des ruissellements de production de sulfate, carbonate, nitrate et chlorure. Les ruissellements de sulfate et de carbonate sont produits à partir du traitement classique tandis que les ruissellements de nitrate de chlorure seraient produits selon un nouveau procédé maintenant étudié à CANMET pour le traitement des minerais complexes à basse teneur.

Les objectifs du programme sont:

1. Donner une critique de la documentation sur l'isolement et sur les méthodes chimiques-analytiques, pour l'enlèvement des radionucléides des liqueurs de chlorure, sulfate, nitrate et carbonate.
2. Passer en revue les principes de chimie sur les radionucléides Ra^{226}, Th^{230} et Pb^{210}.
3. Préparer un sommaire des coûts de premier établissement et d'opération pour l'élimination et l'isolement des radionucléides par des procédés sélectionnés.
4. Déterminer la meilleure technologie et ses chances de réussite technique pour la mise en oeuvre des circuits d'isolement et/ou d'élimination afin de minimiser les teneurs de radionucléides provenant de procédés actuels et autres.
5. Proposer un plan de recherche pour l'évaluation en laboratoire des autres méthodes d'isolement et/ou d'élimination.

Les travaux du contrat ont été effectués par le premier auteur, I.J. Itzkovitch de la Division de la métallurgie de l'Ontario Research Foundation. G.M. Ritcey du Laboratoire du traitement des minerais, Laboratoires des sciences minérales de CANMET, le second auteur, a agit en tant que conseiller technique pour le contrat (22SQ-23440-7-9116) avec l'Ontario Research Foundation. Le rapport préparé par l'adjudicataire a été soumis dans sa présente forme afin d'être disponible au public dans le plus bref délai.

D.A. Reeve
Directeur
Programme de recherche sur l'énergie

REMOVAL OF RADIONUCLIDES FROM PROCESS STREAMS - A SURVEY

by

I.J. Itzkovitch* and G.M. Ritcey**

ABSTRACT

This report details the origin and control of radium 226, thorium 230 and lead 210 contamination of mill effluent streams from conventional and non-conventional milling of uranium ores, reviews the basic chemistry of the radionuclides as it relates to potential alternatives for control and presents these alternatives along with a summary of published cost data.

The conclusions from the study indicate that the current technology, using sulphuric acid processing, solubilizes only a comparatively small quantity of the radionuclides, with the solid tailings containing approximately the same concentration as the original ore.

Present technology does not provide for complete removal and isolation of the radionuclides. Current practice for control of thorium 230 in liquid effluents by neutralization is adequate to meet present Governmental guidelines. Radium in solution is presently being controlled by precipitation with barium chloride but levels of less than 3 pCi/L of soluble radium could be difficult if not impossible to achieve consistently by this treatment. A specification limit of 10 pCi/L would appear possible to achieve, but such a target level of 10 pCi/L for a total radium in tailings effluent will not be attained by simple settling of barium radium sulphate. Additional technology may be required although the use of flocculants appears promising. Indications are that the concentration of lead 210 in liquid effluent may exceed present guidelines. No specific control procedures are employed for lead 210.

The leaching characteristics of the radionuclides from solid tailings are such that on mill shutdown, seepage and run-off will have to be treated to prevent environmental contamination. Alternatives include

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processing of tailings to reduce the radionuclide concentration or using different process technology that would be economically and environmentally acceptable for the processing and recovery of uranium from ores. These technologies are in the early stage of development. A level of 50 pCi/g radium 226 in final tailings appears attainable in practice; one process produces a level of 10-20 pCi/g.

Methods of isolating radium 226 are required for treating effluents from conventional milling as well as from alternative processes under development. Ion exchange is suggested as a means of isolating these radionuclides.

ENLEVEMENT DES RADIONUCLEIDES
DES ECOULEMENTS DE PRODUCTION - UNE ETUDE

par
I.J. Itzkovitch* et G.M. Ritcey**

RESUME

Le présent rapport décrit l'origine et la maîtrise d'une contamination par le radium 226, le thorium 230 et le plomb 210 des effluents d'usine provenant de la trituration classique ou non des minerais d'uranium, passe en revue la chimie fondamentale des radionucléides ayant trait aux alternatives possibles de maîtrise et présente ces alternatives accompagnées d'un sommaire de données de coûts publiées.

On doit conclure de l'étude que la technique récente utilisant le traitement à l'acide sulfurique ne dissout qu'une quantité relativement petite de radionucléides et que les stériles solides contiennent à peu près la même concentration que le minerai d'origine.

La technologie actuelle ne peut atteindre l'enlèvement et l'isolement complets des radionucléides. La pratique actuelle de maîtise du thorium 230 dans les effluents liquides par la neutralisation rencontre les normes exigées par le gouvernement. En ce moment, le radium dans la solution est maîtrisé à l'aide de la précipitation avec le chlorure de baryum. Des concentrations de moins de 3 pCi/L de radium soluble peuvent être difficiles sinon impossibles à atteindre par cette méthode de façon cohérente. Les limites prescrites de 10 pCi/L semblent réalistes mais un tel niveau de radium dans les effluents de stériles ne peut être obtenu par un simple dépôt sédimentaire de sulfate de baryum et radium. L'usage de floculants semble

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intéressant. Tout indique que la concentration de plomb 210 dans l'effluent liquide pourrait dépasser celle qui est inscrite dans les directives. Aucun procédé spécifique de maîtrise est employé pour le plomb 210.

Les caractéristiques de lixiviation des radionucléides à partir des stériles solides sont telles qu'à la fermeture de l'usine, les écoulements et les ruissellements devront être traités afin de prévenir une contamination de l'environnement. Les méthodes alternatives comprennent le traitement des stériles afin de diminuer la concentration de radionucléide ou l'utilisation d'une autre technologie pour la récupération de l'uranium du minerai. Ces technologies en sont aux premiers stades de développement. Un niveau de radium 226 de 50 pCi/g dans les derniers stériles semble être réalisable; une méthode prétend atteindre un niveau de 10-20 pCi/g.

Les méthodes d'isolement du radium 226 sont requises pour le traitement d'effluents provenant de la trituration classique aussi bien que de d'autres procédés en développement. L'échange d'ions a été suggéré comme moyens d'isoler ces radiocléides.

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INTRODUCTION

The Canadian Uranium industry experienced a rapid growth in the postwar period. Twenty-eight mines and nineteen mills were brought into production in the Elliot Lake and Bancroft areas of Ontario, at Beaverlodge, Saskatchewan and in the Northwest Territories, during the period from 1948 to 1958. As rapid as was the growth, so was the industry's subsequent decline in the early sixties. Most of the mines and mills closed down and all research and development capabilities and facilities in both the private and public sector were allowed to decline. Canadian producers and former producers are listed in Table 1 (1).

Increased demand and the subsequent rise of uranium oxide prices has resulted in a world-wide rejuvenation of the uranium industry. Annual world demand for uranium is expected to increase 12- to 15-fold in the next 25 years with annual requirements of between 200,000 and 300,000 metric tons of uranium anticipated by the year 2000 (2).

Canada is in the unique position of being both a major consumer and exporter of uranium. Stability of the Canadian uranium industry appears ensured to at least the year 2000. Federal government guidelines for uranium exports require that sufficient uranium be reserved for domestic needs to enable each nuclear reactor, now producing or planning for production ten years into the future, to operate at an average annual rate of 80% of its capacity for 30 years. To meet this guideline, expansion of the uranium industry's production capabilities from the current 7000 metric tons annually to some 13000 metric tons by the year 2000, is required. (2).

TABLE 1

CANADIAN URANIUM PRODUCERS AND FORMER PRODUCERS

Original Corporate Name and Mine Location	Mill Capacity (tons/day)	Mill Production Commenced	Ceased Production	Remarks
Elliot Lake district, Ont.				
Algom Uranium Mines Ltd.				Amalgamated with Rio Algom Mines Ltd.
Nordic mine	3,700	Jan. 1957		
Quirke mine	3,000	Oct. 1956	Jan. 1961	
Can-Met Explorations Ltd.	3,000	Nov. 1957	Apr. 1960	Amalgamated with Denison Mines Ltd.
Cons. Denison Mines Ltd.	6,000	June 1957		Name changed to Denison Mines Ltd.
Milliken Lake Uranium Mines Ltd.	3,000	Apr. 1958	June 1964	Amalgamated with Rio Algom Mines Ltd.
Northspan Uranium Mines Ltd.				Amalgamated with Rio Algom Mines Ltd.
Buckles mine	no mill	Early 1957	Oct. 1958	
Lacnor mine	4,400	Nov. 1957	July 1960	
Panel mine	3,000	Mar. 1958	June 1961	
Spanish American mine	2,000	May 1958	Feb. 1959	
Pronto Uranium Mines Ltd.	1,500	Oct. 1955	Apr. 1960	Amalgamated with Rio Algom Mines Ltd.
Stanleigh Uranium Mining Corp Ltd.	3,300	Apr. 1958	Jan. 1961	Amalgamated with Preston Mines Ltd.
Stanrock Uranium Mines Ltd.	3,300	Apr. 1958		
Bancroft area Ont.				
Bicroft Uranium Mines Ltd.	1,400	Nov. 1956	June 1963	Amalgamated with Macassa Gold Mines Ltd.
Canadian Dyno Mines Ltd.	1,200	May 1968	June 1960	
Faraday Uranium Mines Ltd.	1,200	Apr. 1957	June 1964	Name changed to Metal Mines Ltd.
Greyhawk Uranium Mines Ltd.	no mill	Sept. 1957	Apr. 1959	
Beaverlodge area, Sask.				
Black Bay Uranium Ltd.	no mill	Feb. 1958	Early 1960	
Cayzor Athabaska Mines Ltd.	no mill	Feb. 1957	Mar. 1960	
Cons. Nicholson Mines Ltd.	no mill	Feb. 1955	Apr. 1956	
Eldorado Mining & Refining Ltd.	2,000	Apr. 1953		
Gunnar Mines Ltd.	2,000	Sept. 1955	Feb. 1964	Name changed to Gunnar Mining Ltd.
Lake Cinch Mines Ltd	no mill	May 1957	Mar. 1960	
Lorado Uranium Mines Ltd.	750	May 1957	Apr. 1960	
National Explorations Ltd.	no mill	Apr. 1955	Oct. 1958	
Nesbitt LaBine Uranium Mines Ltd.	no mill	Sept. 1954	June 1955	
Rix-Athabaska Uranium Mines Ltd.	no mill	Apr. 1954	June 1960	Amalgamated with Rio Algom Mines Ltd.
Northwest Territories				
Eldorado Mining & Refining Ltd.				
Port Radium mine	300	Aug. 1943	Sept. 1960	
Rayrock Mines Ltd.	150	June 1957	July 1959	

This need for rapid expansion has resulted in a strong resurgence across Canada of uranium prospecting and processing as well as Research and Development. Current and planned Canadian uranium mill facilities in Canada are given in Tables 2 and 3 (3).

Increasingly, concerns about the environmental impact of existing and proposed uranium ore mining and milling operations have been expressed. This is exemplified by the requirement to assess any impact which could result from an expansion of mining and milling facilities by Denison Mines Ltd. and Rio Algom Mines Ltd. in Elliot Lake, Ontario and by the Royal Commission review in Saskatchewan on the proposed Mining development at Cluff Lake. (4).

The mining and milling of uranium ores is unique in as much as it involves the handling and disposal of large amounts of low level radioactive material.

The average grade of uranium bearing ore has been reported to be 0.22 percent uranium oxide in the U.S.A. (5) and 0.1% for the proposed expansion at Elliot Lake, Ontario (6). Milling of high grade ores (>1% U_3O_8) is being considered for Northern Saskatchewan.

Uranium 238 (99.28% of the total uranium) has an alpha activity of 152 microcuries per pound. Assuming uranium ore to be in the secular equilibrium, the total alpha activity would be about 8 times the activity associated with a pound of uranium 238 or 1,216 microcuries per pound of uranium 238. As only uranium is recovered from the ore, the other radioactive members of the family

TABLE 2

EXISTING CANADIAN URANIUM MILLS (1979)

BASIC PROCESS	MILL	COMPANY	LOCATION	START UP DATE	ORE CHARACTERISTICS		LEACH
					TYPE	U MINERAL	
ACID LEACH COUNTER CURRENT DECANTATION ION EXCHANGE	Quirke	Rio Algom	Elliot Lake Ontario	1957	Quartz-Pebble Conglomerate	Uraninite Brannerite	Single stage acid
	Rabbit Lake	Gulf Minerals	Wollaston Lake, Sask.	1976	Vein Replacement type	Pitchblende	Single stage acid
	Denison	Denison Mines	Elliot Lake Ontario	1957	Quartz-Pebble Conglomerate	Uraninite Brannerite	Single stage acid
ACID LEACH FILTRATION ION EXCHANGE	Madawaska	Madawaska Mines	Bancroft,Ont.	Shut-down'64 Reopen-'77	Pegmatite	Uraninite Uranothorite	Single stage acid
ACID LEACH CONTINUOUS ION EXCHANGE SOLVENT EXTRACTION	Agnew Lake	Agnew Lake Mine S.	Espanola Ontario	1977	Quartz-Pebble Conglomerate	Uranothorite	Stope and Heap Leach
ALKALI CARBONATE LEACH FILTRATION CAUSTIC PRECIPITATION	Beaverlodge	Eldorado Nuclear	Eldorado Saskatchewan	1953	Vein	Pitchblende	Atmospheric Carbonate (small acid leach circuit)

TABLE 3

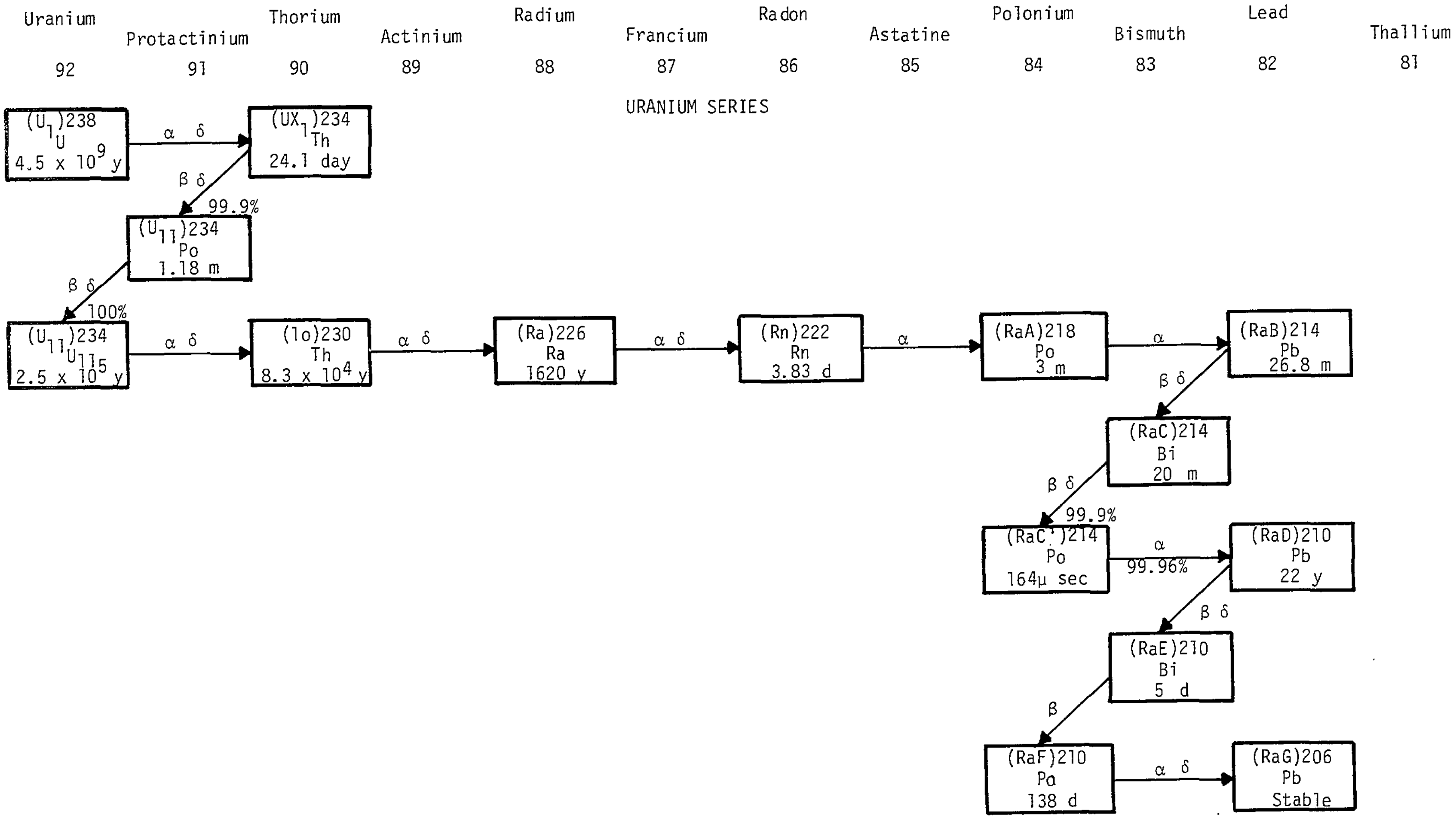
NEW CANADIAN URANIUM MILLS PLANNED

BASIC PROCESS	MILL	COMPANY	LOCATION	START UP DATE	ORE CHARACTERISTICS TYPE	U MINERAL	LEACH
ACID LEACH	Stanrock	Denison	Elliot Lake Ontario	Shutdown'64 Reopen '83?	Quartz-Pebble Conglomerate	Uraninite Brannerite	Single stage acid
ION EXCHANGE	Panel	Rio Algom	Elliot Lake Ontario	Shutdown'61 Reopen'83?	Quartz-Pebble Conglomerate	Uraninite Brannerite	Single stage acid
	Nordic	Preston Mines Rio Algom Managed	Elliot Lake Ontario	Shutdown'70 Reopen ?	Quartz-Pebble Conglomerate	Uraninite Brannerite	Single stage acid
ACID LEACH FILTRATION	Cluff Lake	Amok	Cluff Lake Sask.	1981 ?	Vein Replacement Type	Pitchblende	Single stage acid
ACID LEACH	Key Lake	UEM SMDC ENL	Key Lake Sask	1983 ?	Vein Replacement Type	Pitchblende Nickel Sulphide Nickel Arsenide	Acid Leach under Investigation

are discharged as waste. Therefore, 912 microcuries or 75% of alpha activity per pound uranium recovered, is discharged to tails. For 0.17% uranium ore 1824 microcuries of alpha activity per ton of ore processed is discharged as waste. In addition, an equal amount of beta activity (1824 microcuries) will also be contained in the mill waste.

The containment and ultimate disposal of these mill wastes is of importance because of the biological toxicities of some of the long lived radionuclides present in uranium bearing ores. The naturally occurring uranium isotopes U-238 and U-235 are the respective parents of two series of radioactive daughters shown in Figure 1. The International Commission on Radiological Protection, ICRP, providing advice on the effects from small doses of radiation has set close limits for radiation workers. From these doses maximum permissible concentrations (MPC) of radioisotopes in air and water were derived. MPC water (MPC_w) values for the radioisotopes present in uranium ore are given, in order of decreasing hazards, in Table 4 (7). Hence the isotopes of primary concern are radium 226, lead 210 and thorium 230 having half-lives of 1,622 years, 22 years and 83,000 years respectively.

In Canada, the two major uranium producing Provinces, Ontario and Saskatchewan, have established effluent objectives of 3 p Ci per liter for dissolved radium 226 in tailings pond discharges (6). It has also been recognized that significant quantities of radium could be released to the environment as suspended material. This has led to a proposal by the Atomic Energy Control Boare (AECB) to set "a target of 10 p Ci per liter total radium 226" in tailings pond discharge (8). Control measures to meet these guidelines have not as yet been developed.



sec = seconds
m = minutes
d = day
y = year

FIGURE 1

RADIOACTIVE DECAY CHAINS FOR URANIUM AND THORIUM.

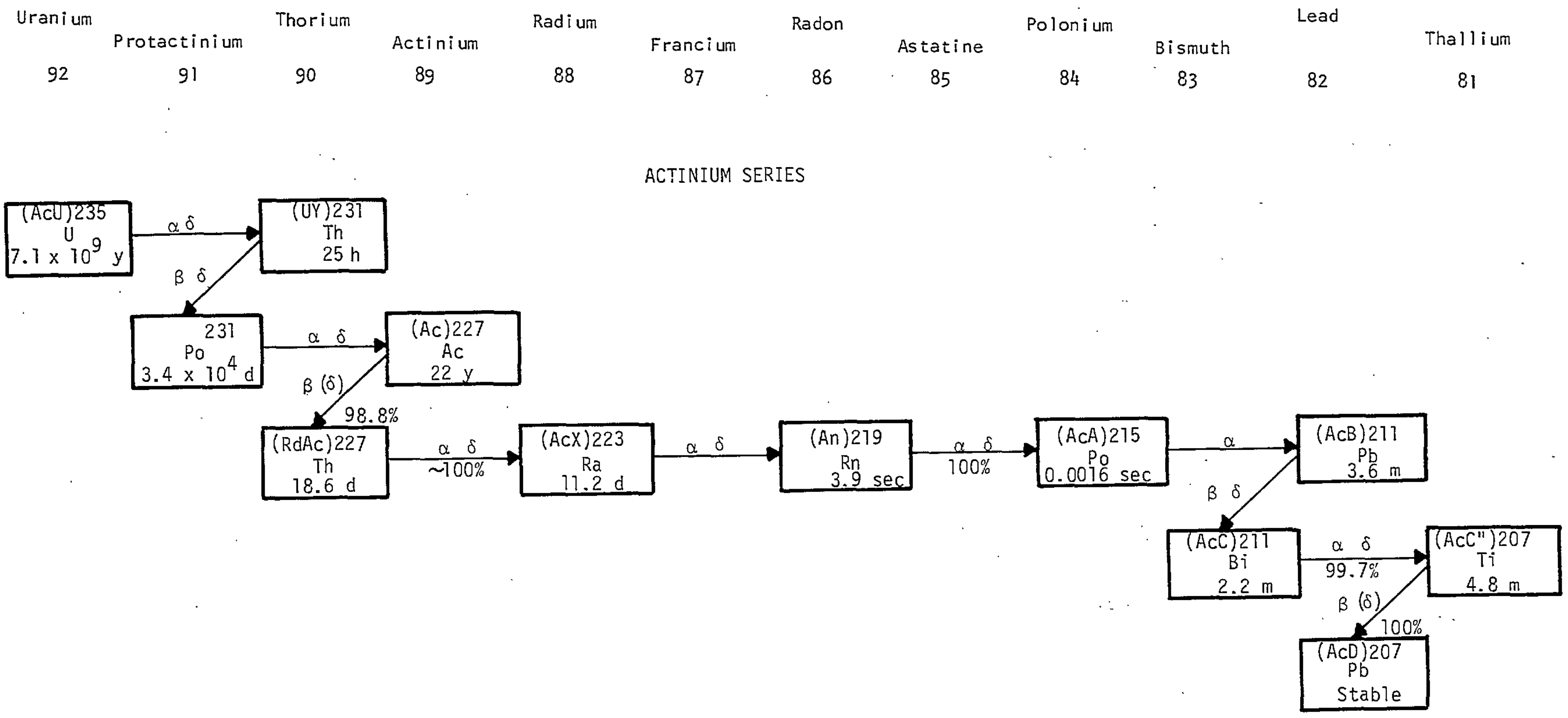


FIGURE 1 (cont'd.)

RADIOACTIVE DECAY CHAINS FOR URANIUM AND THORIUM

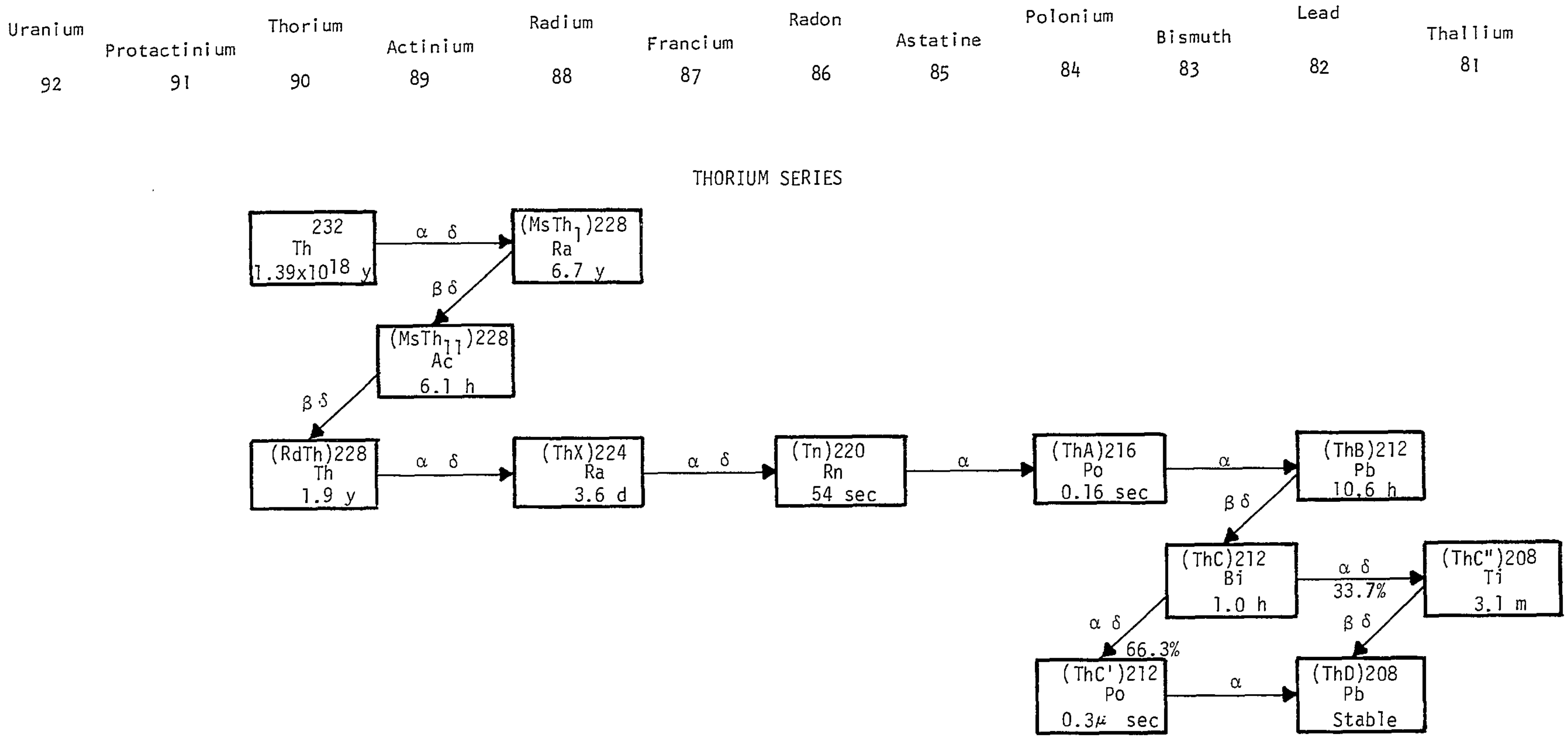


FIGURE 1 (cont'd.)

RADIOACTIVE DECAY CHAINS FOR URANIUM AND THORIUM

sec = seconds
m = minutes
d = day
y = year

Currently uranium mills in Canada control thorium 230 in liquid effluents by neutralization of tailings to pH 9.5. Radium 226 in the liquid effluents is controlled by the addition of barium chloride and in the case of Eldorado Nuclear Ltd., Beaverlodge operation, sulfate is also added. The precipitated barium radium sulfate is then settled, with the settling pond overflow discharged to natural water courses. No specific control procedures for lead 210 are employed by the mills.

Disposal of solid tailings containing un-leached thorium and radium as well as precipitates from effluent treatment pose a long term control problem. Weathering and the generation of slightly soluble radium 226 from its parent thorium 230 will result in continuous dissolution of the radionuclides. Treatment of run-off and drainage water from the tailings areas would be required, even after the site has been abandoned, to prevent contamination of water courses and ultimately drinking water.

Battelle (9), in their summary of radioactive wastes from the commercial nuclear power industry in the U.S.A., estimated that in 1980, 180×10^6 tons of solid uranium mill tailings would be produced annually having a total curie content of 3.3×10^4. Liquid milling effluents were estimated at 20×10^6 tons containing 1.1 curies of radioactivity. The total annual radioactivity disposed of as tailings was reported to be comprised of 9×10^3 Ci radium 226;

TABLE 4

URANIUM-RADIUM FAMILY, MPC_w VALUES[(a)]

Isotope	MPC_w (pc/l)	Critical Organ	Half-life	Emission
Ra^{226}	3.3	Bone	1620 Yr	Alpha
Pb^{210}	33	Kidney	22 Yr	Beta
Po^{210}	233	Spleen	140 d	Alpha
Th^{230}	667	Bone	8×10^4 yr	Alpha
Th^{234}	6667	GI tract	24.1 d	Beta
U^{234}	10000	GI tract	2.5×10^5 yr	Alpha
U^{238}	13300	GI tract	4.5×10^9 yr	Alpha
Bi^{210}	13300	GI tract	5 d	Beta
Pa^{234}	(b)	-	1.1 min	Beta
Po^{218}	(b)	-	3.05 min	Alpha
Po^{214}	(b)	-	1.6×10^{-4} s	Alpha
Bi^{214}	(b)	-	19.7 min	Beta
Pb^{214}	(b)	-	26.8 min	Beta
Rn^{222}	(gas)	Lung	3.8 d	Alpha

(a) MPC_w value is the maximum permissible concentration in water, for average member of the general population (1/30th ICRP value for continuous occupational exposure).

(b) No value given.

6×10^3 Ci thorium 230; 2×10^3 Ci lead 210 and 2×10^3 Ci polonium 210. Translating the above to the Canadian scene for the year 2000, when 13000 metric tons of uranium will be required, about 10% of the above wastes will be generated annually, assuming an average ore grade of 0.1% U_3O_8.

Thus one of the environmental concerns is the control of radium 226 and other radionuclides during the operating life of the mine-mill complex. Of equal or greater concern is the long term effects and control of radionuclides which enter the environment from tailings disposal areas after the site has been abandoned.

The following report details the origin and control of radionuclide contamination of mill effluent streams from conventional and non-conventional milling of uranium ores, reviews the basic chemistry of the radionuclides of concern as it relates to potential alternatives for control, presents these potential alternatives along with a summary of published cost data. A research plan for investigating these alternatives was presented separately to CANMET.

SECTION 1 - CONVENTIONAL MILLING OF URANIUM ORES

1.1 MILL PROCESSES

The source and nature of radionuclide contamination of effluent streams from uranium processing operations is dependent on the chemical processes employed to recover the uranium. A general description of the commercial uranium milling processes is given below. Detailed description of the mills, circuits, equipment etc. are given in references 11-16.

The process employed to extract uranium from its ores depends to a large extent on ore minerology. Basically, two processes are in commercial use today. These are based on sulfuric acid leaching and carbonate leaching of uranium ore. Simplified flowsheets for these processes are given in Figures 2 and 3.

Unit operations basic to both processes are crushing, grinding, leaching, wherein uranium is dissolved from the ore, solid-liquid separation and uranium recovery. For acid leaching, the last process steps involve the selective removal of uranium from the leach liquor by ion exchange or solvent extraction as well as the precipitation of product yellowcake. In carbonate leach flowsheets the yellowcake is precipitated directly from the clarified leach liquor.

A general description of the individual unit operations is given below:

ACID LEACHING PROCESS

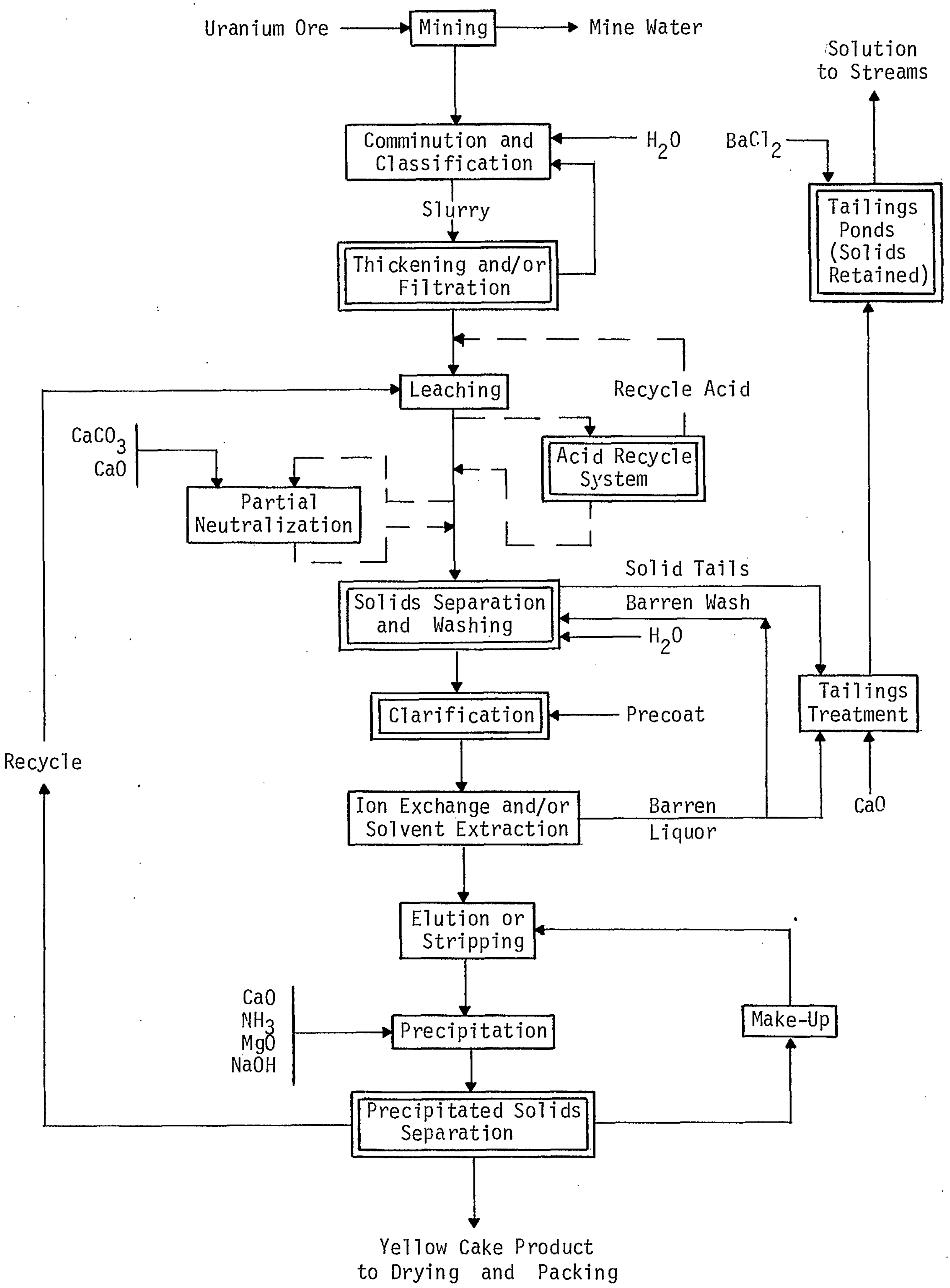


FIGURE 2

CARBONATE LEACHING PROCESS

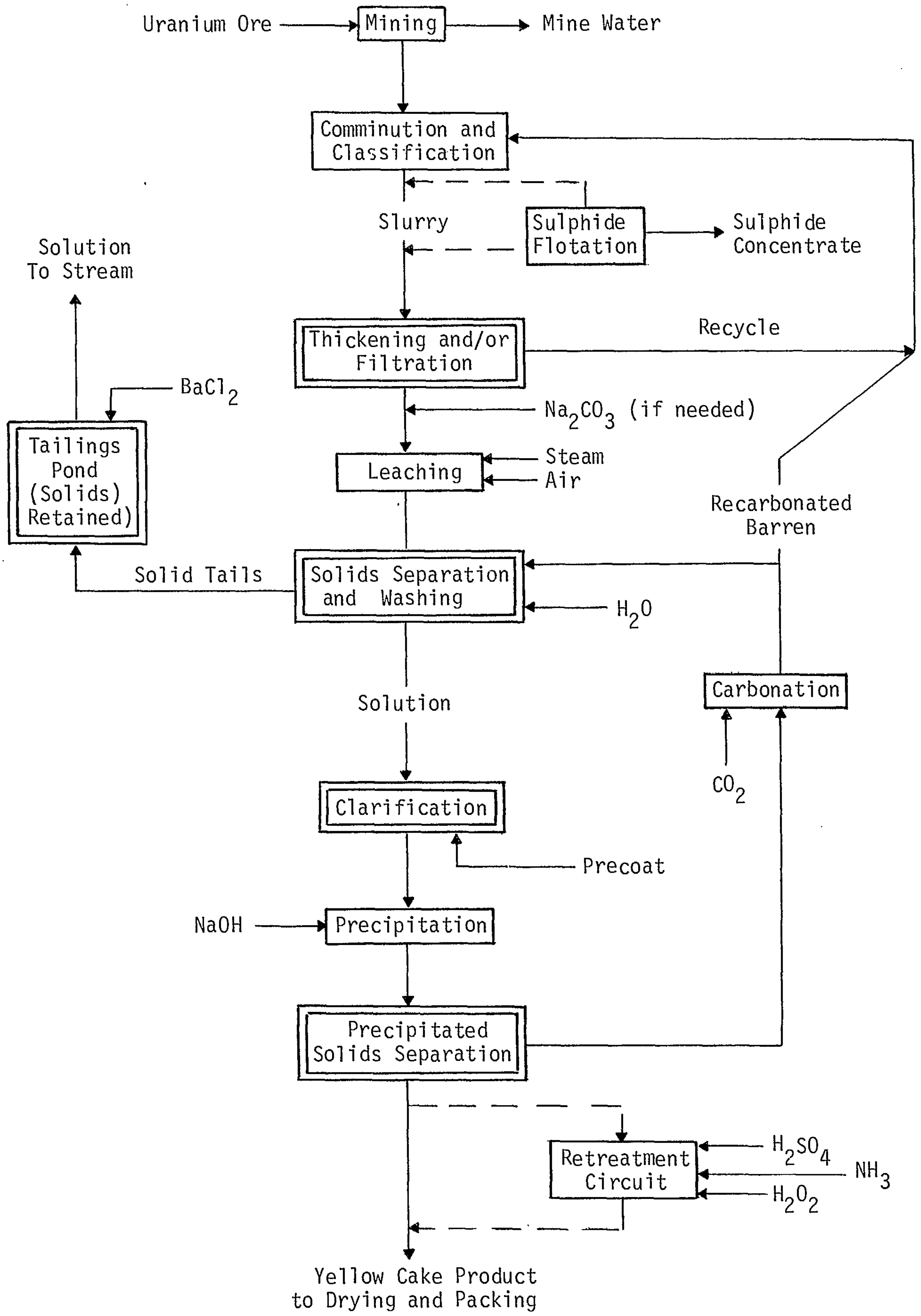


FIGURE 3

Crushing

Crushing is carried out to reduce the ore to a size suitable for wet grinding (0.5 to 0.75 inch). Crushing operations are dry and are provided with dust control equipment.

Grinding

Grinding is carried out to reduce the ore size to allow for efficient leaching of the uranium minerals. Optimum grind takes into account both the uranium liberation size and solid-liquid separation problems that may occur if the ore is ground too fine. In general, for acid leaching, U.S. Sandstones are ground to 30-40% -200 mesh whereas Canadian and Australian ores containing brannerite and monazite require a finer grind (55 to 65% -200 mesh) (16).

Grinding in most mills is carried out wet. Water is added to the ore as it enters the mill. Grinding water may be recycled mill solution, mine water, fresh water or a combination of these. After classifying the solids may be thickened to a solids density suitable for leaching. Rejected grinding water is usually reused in the grinding circuit.

Leaching

Leaching is the first chemical process in the mill. The processes prior to leaching involve physical preparation of the ore to produce a material suitable for uranium extraction.

SULFURIC ACID LEACHING, is carried out at ambient to 60°C, by contacting the ground ore slurry with acid in a quantity sufficient to extract the uranium while at the same time minimizing gangue dissolution. Oxidant, usually sodium chlorate is added to give a solution potential of about 400 mV so as to oxidize uranium (4+) minerals to the readily soluble uranyl ion. Sulfuric acid consumption is usually in the range 40 to 120 lbs. per ton ore and chlorate consumption from 1 to 3 lbs. per ton ore (16).

ALKALINE CARBONATE LEACHING, is carried out where the ore has a high calcite content making the acid requirements for leaching excessive. The ground ore slurry is reacted at temperatures ranging from 75 to 95°C under atmospheric or pressure conditions with a solution containing sodium carbonate-sodium bicarbonate. Air or oxygen is used as oxidant for uranium (4+) (16).

Currently, the majority of the world's uranium mills have, and continue to employ the sulfuric acid leach process. Of the 27 uranium mills operating in the U.S.A. in 1961, 21 leached the ore with sulfuric acid and the remaining 6 used a sodium carbonate leach (17). In Canada all uranium mills with the exception of the

Eldorado Nuclear Ltd. operation at Beaverlodge, Saskatchewan employed sulfuric acid. The predominance of the processing of uranium ores by acid leaching continues today with the exception of in-situ processing in Texas and the alkaline leach circuit of Rio Algom at Lisbon, Utah, and United Nuclear Homestake at Grants, New Mexico.

Solid-Liquid Separation

Uranium solubilized by leaching is separated from the spent ore solids by physical means such as hydrocycloning filtration and/or thickening. The unreacted solids are washed free of uranium using recycle yellowcake precipitation liquor, other process water, tailings pond water or fresh water. The washed solids are discharged to the tailings pond.

Some mills segregate the sands (coarse material mesh) and slimes (fine material mesh) in the solid-liquid separation step (17). In all cases the sand and slimes are recombined and discharged together to tailings.

Because of the low levels of uranium in the ore on average of 99.8% or 1,998 lbs. per ton of mill feed is discharged to tails.

Uranium Recovery

Having solubilized the uranium values from the ore and separated the solution from the waste solids, what remains is to recover the uranium in a form and purity acceptable for the production of nuclear reactor fuel.

ACID LEACHING is a non-selective process. Large volumes of low-grade liquors (1 gpl U_3O_8) are produced, having a high concentration of impurities. In order to produce a high-grade uranium product from these liquors uranium is recovered and separated from the impurities by adsorption onto selective ion-exchange resins or extracted selectively by solvent extraction reagents. In some plants a combination of ion exchange/solvent extraction process is used, e.g., Eluex Process, as practiced at Agnew Lake (Figure 4) (18) and various plants in South Africa.

Ion exchange and solvent extraction both involve the selective removal of uranium from the dilute leach liquors by adsorption of anionic uranyl sulfate complexes. Strong base anion exchange resins based on a quarternary amine functional group are commercially used whereas solvent extraction employs for the most part tertiary amine solvents. In the past phosphoric acid extractants have also been employed in the solvent extraction circuit (17).

The barren solution, after essentially all the uranium has been recovered, is usually neutralized with lime and discharged to tailings with a small percentage being returned to process.

Once the resin becomes saturated or the solvent loaded the uranium is desorbed or stripped to produce a highly concentrated relatively pure uranium solution. Resin elution is by contact with acidified nitrate or chloride solutions. Acidified sulfate is used as eluting agent in the Eluex Process. Stripping of

ELUEX PROCESS

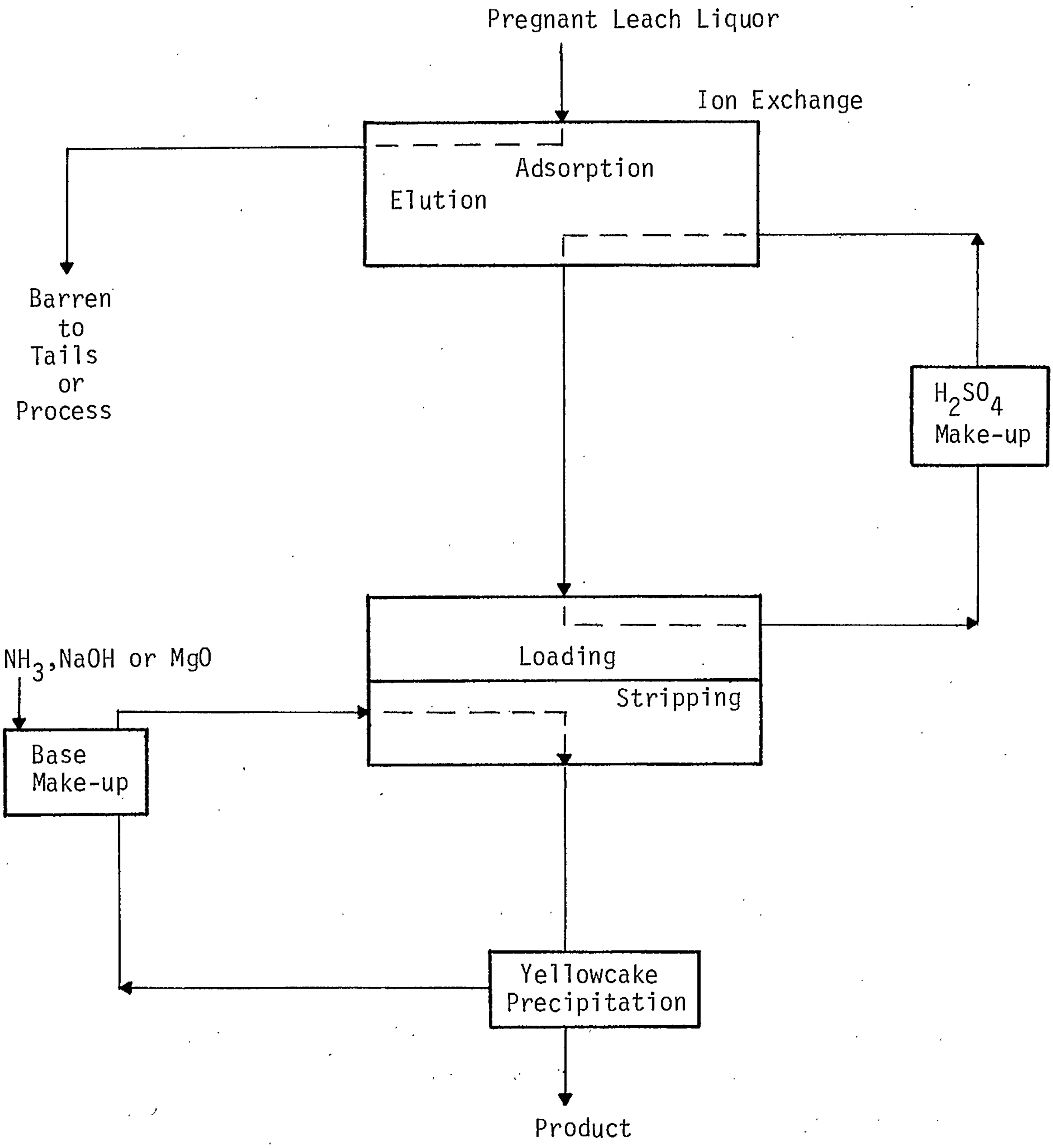


FIGURE 4

loaded solvent is by contact with base. Selective stripping, using NaCl for example for uranium, is employed if molybdenum has been co-extracted, followed by alkaline stripping for molybdenum removal. In both processes recycle liquor, from yellowcake precipitation after make-up is used to elute or strip loaded uranium. Impurities in the recycle strip liquor are controlled by bleeding a portion of the liquor back to the front end of the process. The bleed solution eventually finds its way to the tailings pond.

Following elution or stripping of the uranium from the resins or solvent, the product solution is treated with ammonia, magnesia, lime or caustic to pH 12 to precipitate product yellowcake. The insoluble precipitate is recovered, filtered, dried and packaged for shipment to a refiner.

CARBONATE LEACHING produces a relatively pure uranium leach liquor from which yellowcake is recovered directly by precipitation with caustic. Impurities are controlled by bleeding a portion of the uranium free precipitation liquor to solids washing in the solid-liquid separation unit operation. This liquor finds its way along with the unreacted leach solids to the tailings pond.

I.2 RADIONUCLIDE BEHAVIOUR IN MILLING CIRCUITS

In order to assess the potential for isolating radionuclides in a mill flowsheet by their extraction, either during an intermediate processing step or from the final tailings solution, it is important to review the distribution of radium 226, thorium 230 and lead 210 in conventional uranium milling processes.

In 1962 in-plant surveys were conducted in uranium mills representing typical processing methods (11-14). Findings from these studies have been used to prepare a waste guide for the milling of uranium ores (17). While the milling processes have changed to some extent with improvements in technology, the processes used today are basically the same as those used in 1962. Recent mill surveys (10A,34) show basically the same trend as those surveys conducted 16 years ago.

1.2.1 RADIONUCLIDE DISTRIBUTION IN URANIUM MILLING

The main objective of these in-plant surveys was to determine the radium distribution throughout the mill process (11).

The published data are summarized below:

SULFURIC ACID LEACHING of uranium ores containing 0.2 to 0.5% U_3O_8 (490 to 680 p Ci per g radium 226) was reported to dissolve 0.13 to 0.65% of the radium contained in the ore (17). Others (10,20) have reported radium dissolution from 2.0 to 6.6%. The reason for the lack of agreement is not apparent. In one plant where vanadium is recovered along with uranium by roasting the ore with chloride followed by water leaching of the roasted product, 1.53% of the radium dissolved (12).

Following radium 226 through the mill flowsheets show that no concentration of the radium occurs during uranium recovery from leach liquors by strong base ion exchange or solvent extraction with D_2EHPA (12).

Product yellowcake is reported to contain from 0.02 to 0.25% of the ore radium.

The remainder of the radium, 99.74 to 99.98%, is discharged to the tailings pond as sands (18-27%), slimes (68-79%) and liquid effluent (0.1 to 6.6%). The slime fraction represents, in general, only a third of the weight of waste solids to tails.

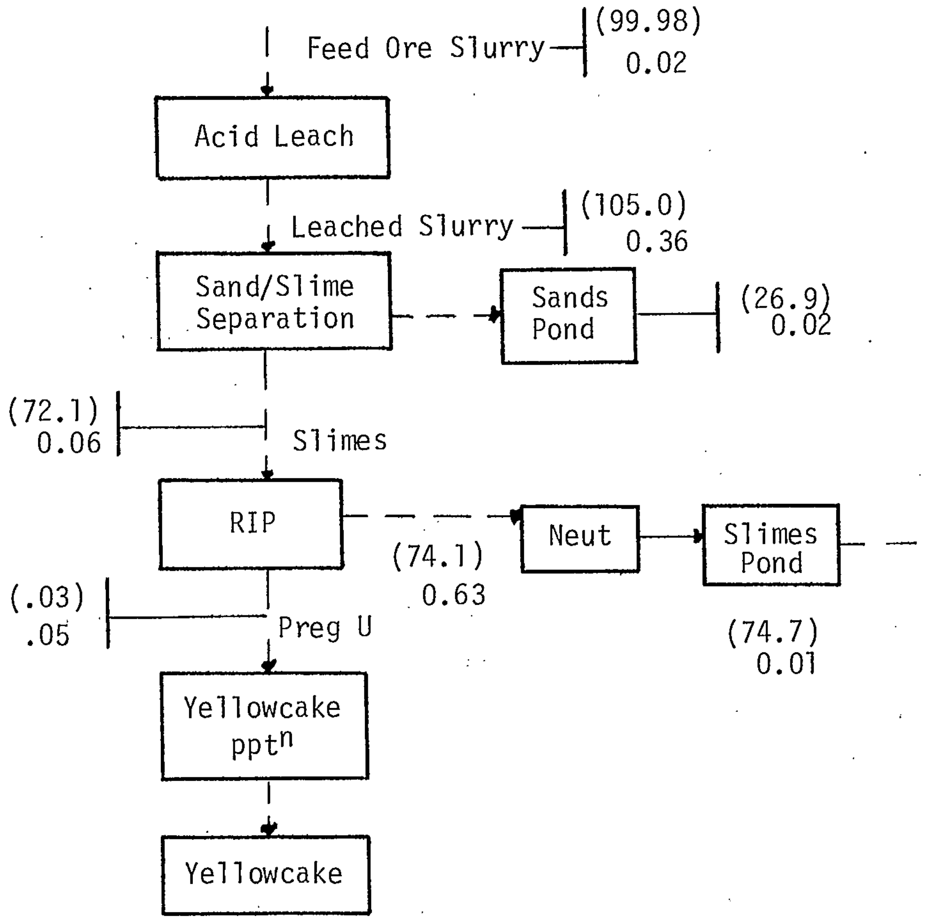
Neutralization of tailings to pH 8 is reported to reduce the soluble radium by 85 to 90% (17).

Simplified acid leach mill circuits and the radium distribution quoted as per cent of feed radium from which the above generalizations were obtained are given in Figures 5 to 7 and summarized in Figure 8.

It is reported that 50% of the ore thorium is dissolved along with the uranium in acid leaching. At Denison Mines Ltd. Elliot Lake, Ontario, mill operating experience has shown that 45% of the thorium is leached (35).

Apparently D2EHPA extracts more thorium than the anion exchange resin. Strong base anion exchange concentration of uranium is reported to co-extract 1% of the total thorium whereas solvent extraction with D2EHPA co-extracts 5% of the feed thorium (11, 12).

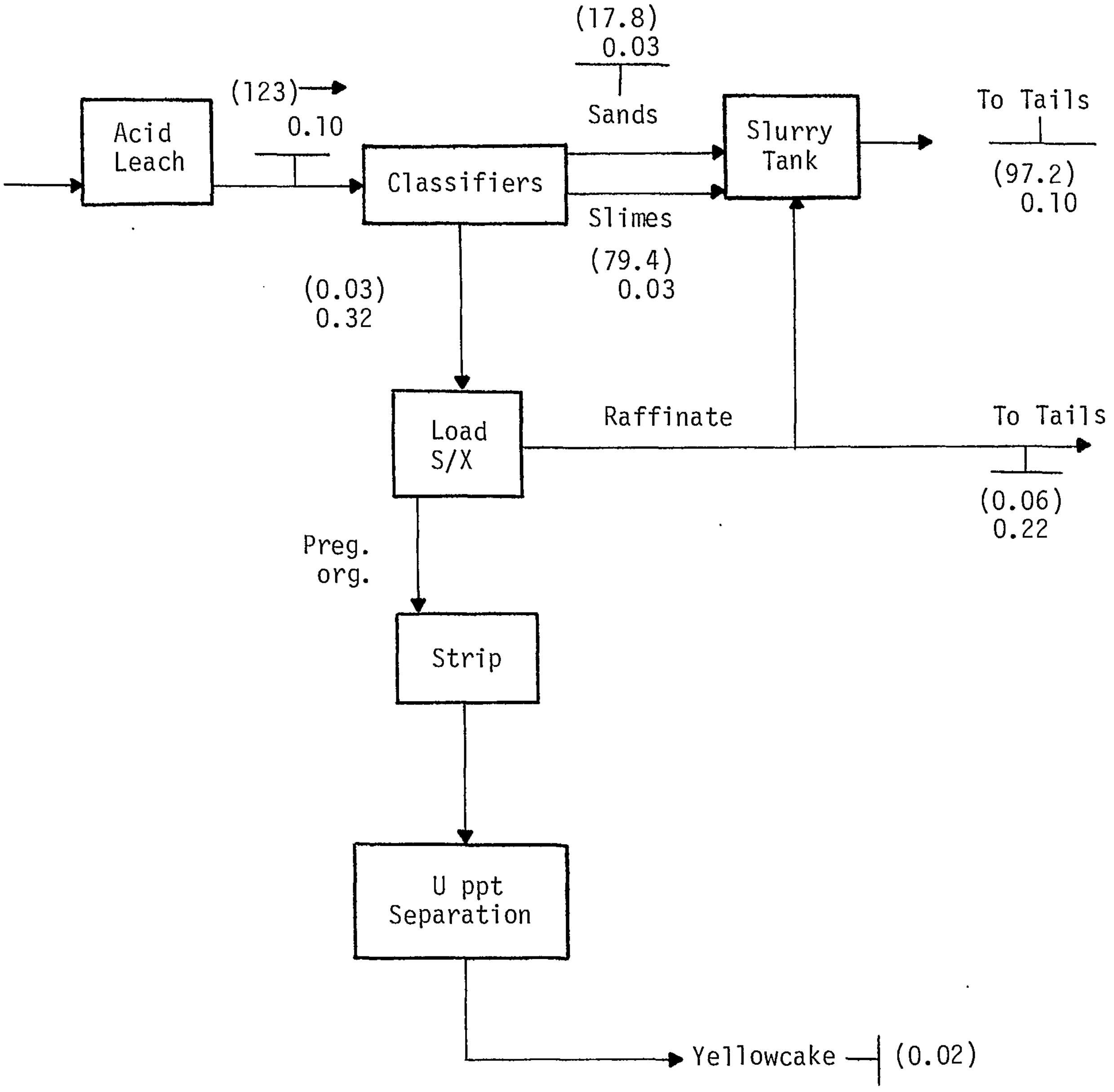
Single stage precipitation of ammonium diuranate gives a yellow-cake containing 1 to 5% of the thorium 230 in the ore (20). Two stage precipitation with lime to control sulfate



( ) Solids

FIGURE 5

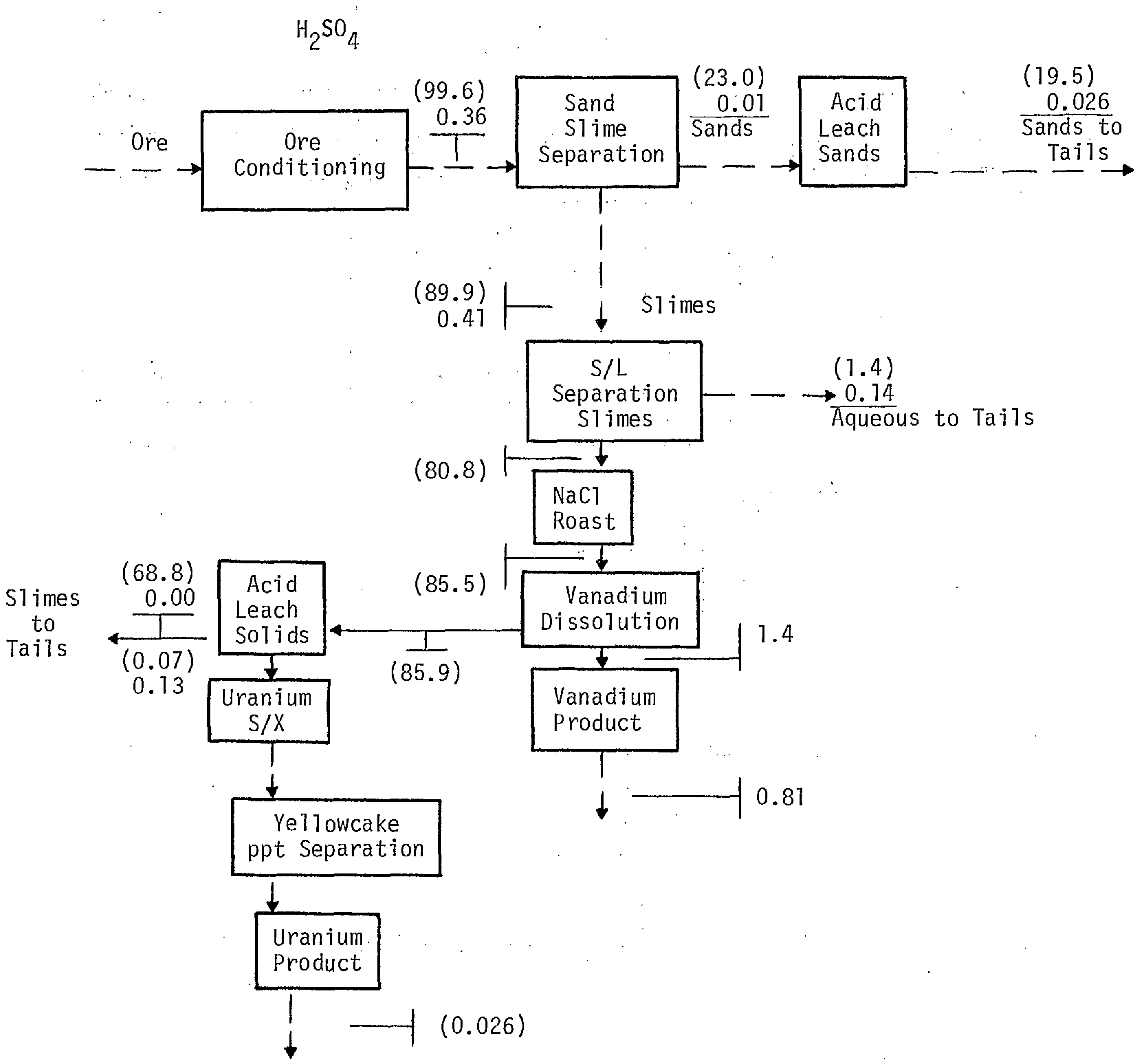
RADIUM DISTRIBUTION IN ACID LEACH-RIP CIRCUIT (15)



( ) Solids

FIGURE 6

RADIUM DISTRIBUTION IN ACID LEACH-SOLVENT EXTRACTION WITH D2EHPA (11)



( ) Solids

FIGURE 7

RADIUM DISTRIBUTION IN ACID LEACH-SOLVENT EXTRACTION WITH D2EHPA AND RECOVERY OF VANADIUM (12)

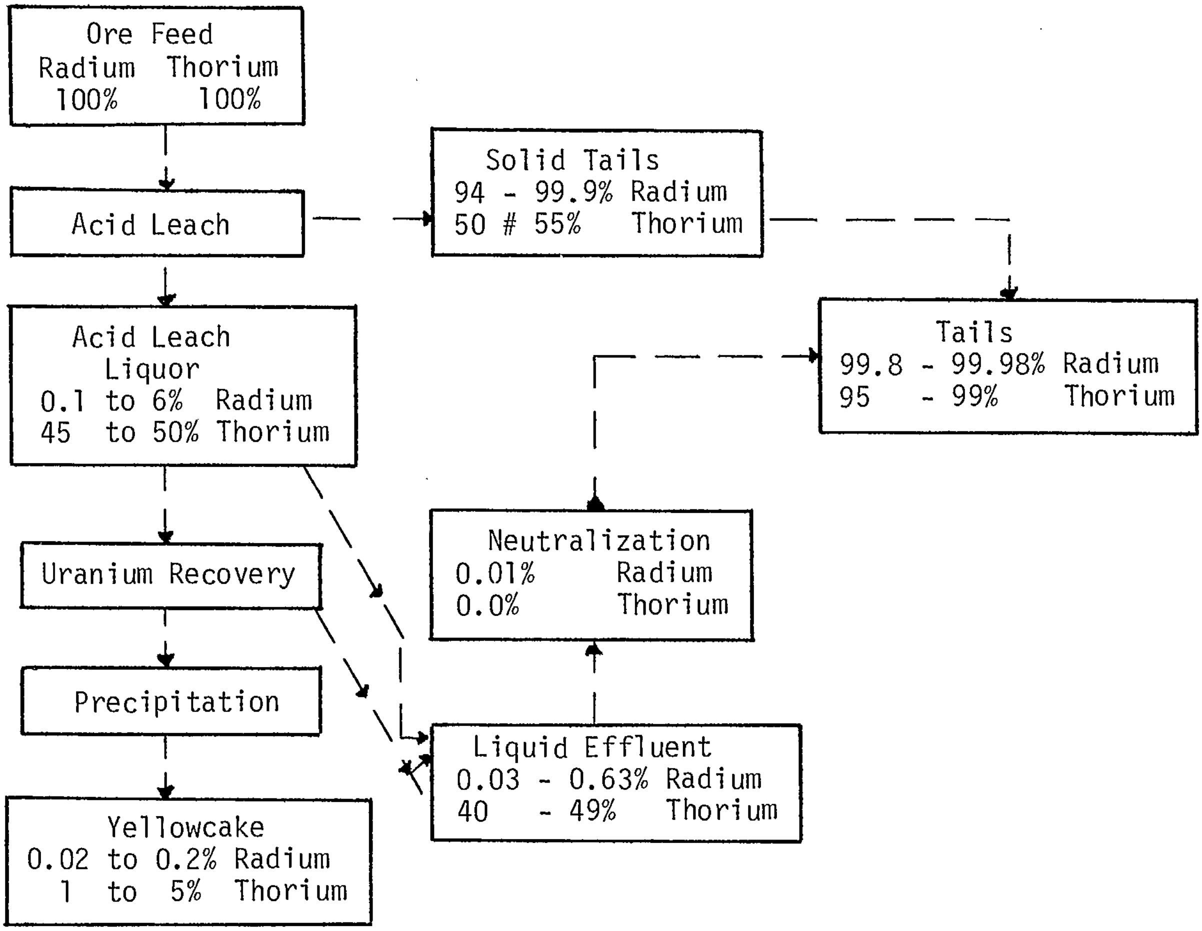


FIGURE 8

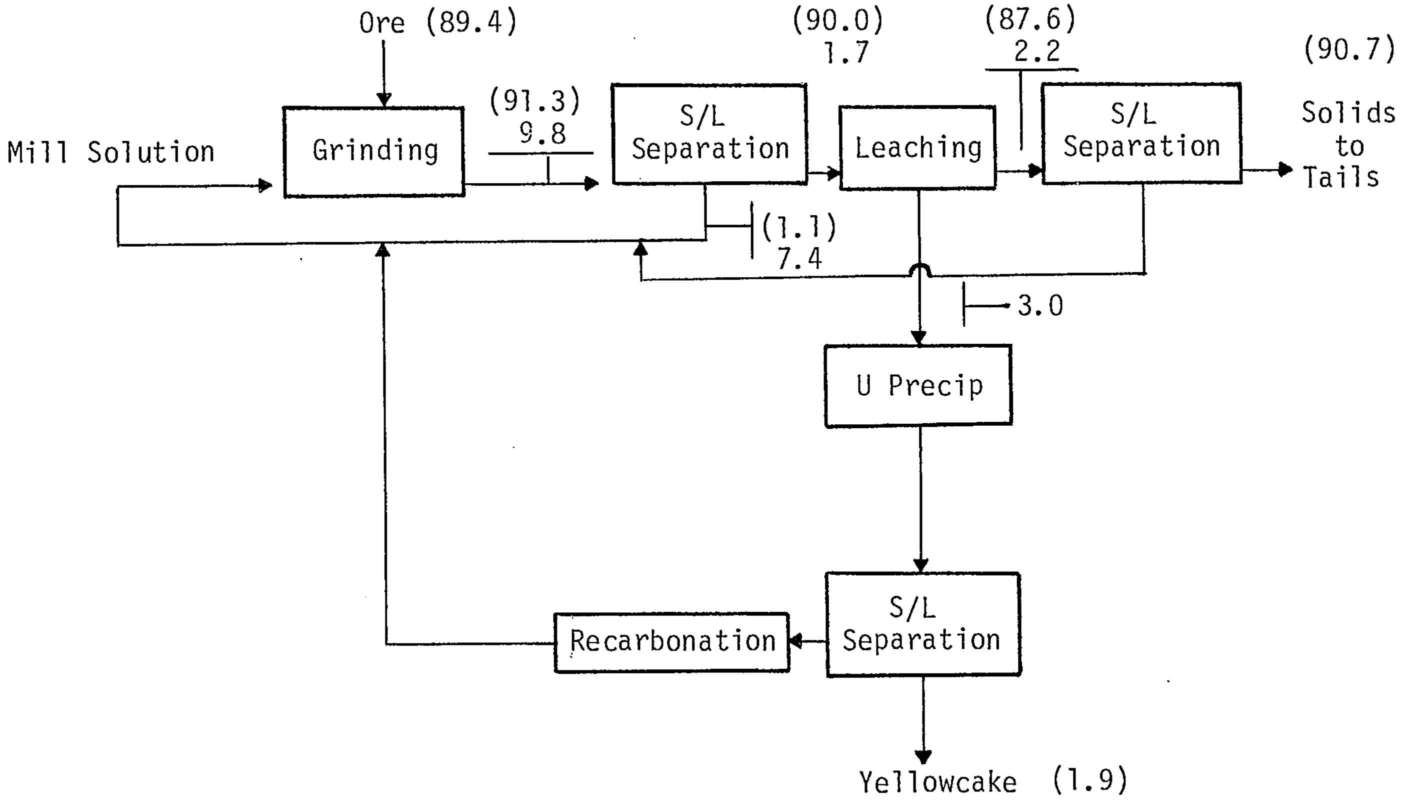
SUMMARY OF RADIUM AND THORIUM BALANCE IN ACID MILL CIRCUITS and adding phosphoric acid to complex the thorium followed by caustic precipitation of yellowcake is claimed to give a uranium product containing less than 0.1% thorium (35).

Tailings neutralization is reported (20) to "reduce soluble thorium to negligible levels." Thus of the feed ore thorium, 50% reports to tailings as unreacted ore and 45 to 49% as hydrolyzed thorium.

No information is available on the distribution of lead 210 in acid mill circuits. Some data have been reported on effluent lead 210 concentrations and these are presented in a subsequent section of this report.

ALKALINE LEACHING of uranium ores containing 0.143 to 0.235% U_3O_8 (420 to 497 p Ci per g radium 226) has been reported to dissolve between 1.5 to 2.2% of the feed radium. (13,14). Others have been reported 2 to 3% (20) and 1.2% (34) dissolution. In no case was thorium dissolution reported. Virtually all the solubilized radium leaves the plant in the yellowcake product. About 0.1% of the feed radium reports in the tailings solution. The remainder 97 to 99% is discharged to the tailings pond as solids.

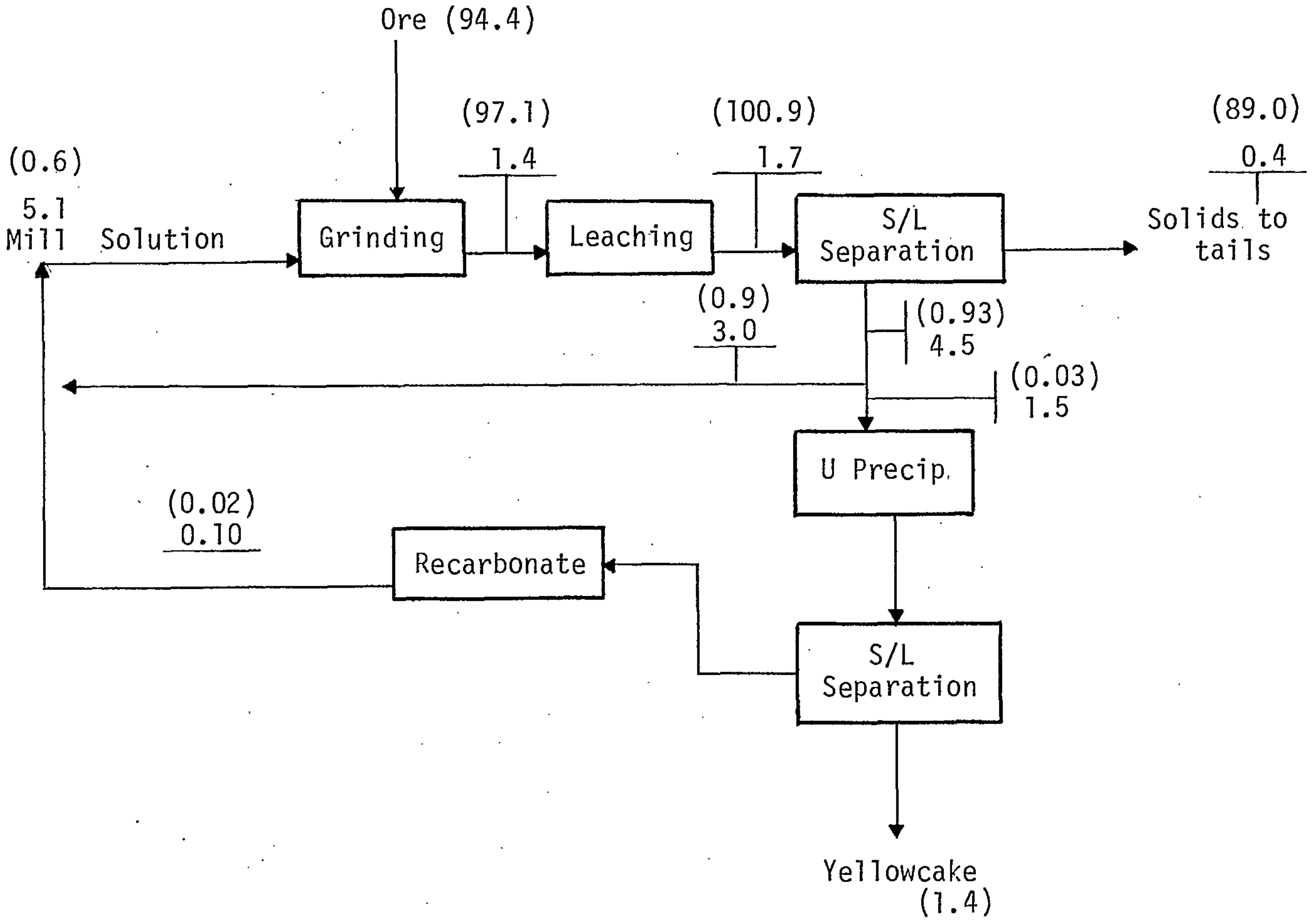
Simplified alkaline mill circuits and the radium distributions quoted as per cent of feed radium are given in Figures 9 to 11 and summarized in Figure 12.



( ) Solids

FIGURE 9

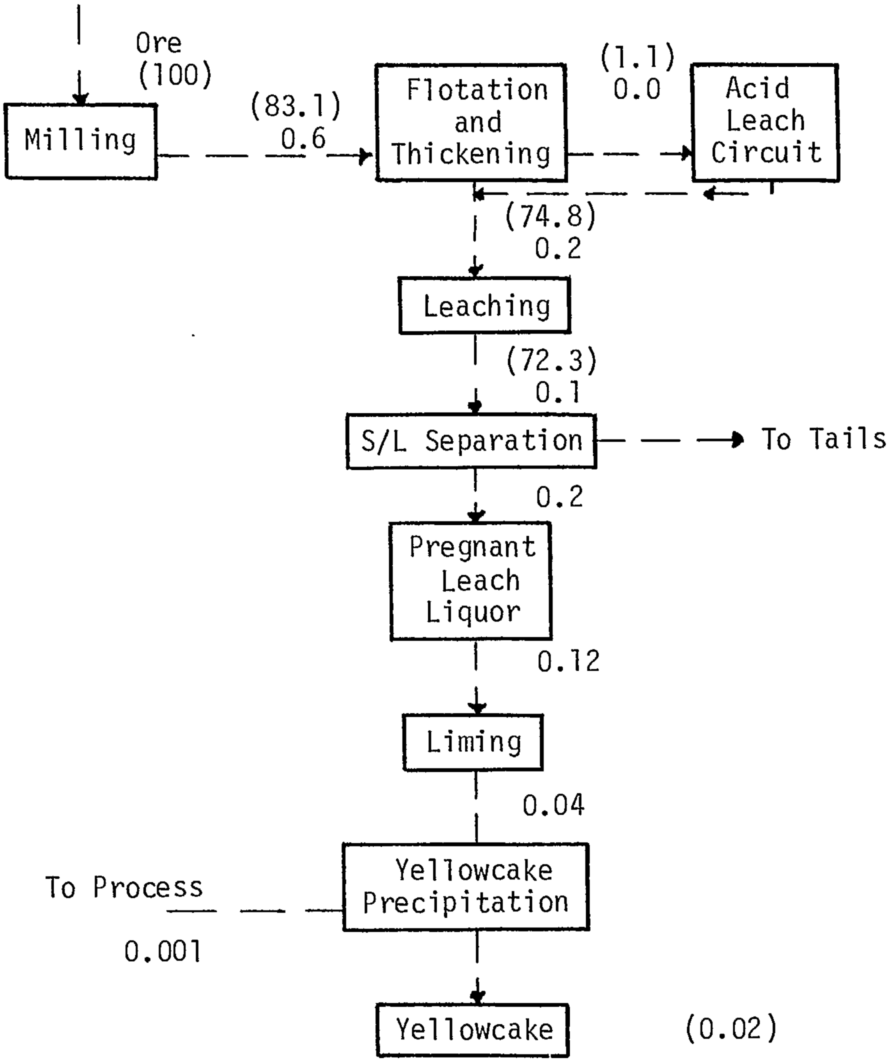
RADIUM DISTRIBUTION IN CARBONATE LEACH CIRCUIT (14)



( ) Solids

FIGURE 10

RADIUM DISTRIBUTION IN CARBONATE LEACH CIRCUIT (13)



( ) Solids

FIGURE 11

RADIUM DISTRIBUTION IN CARBONATE LEACH CIRCUIT (34)

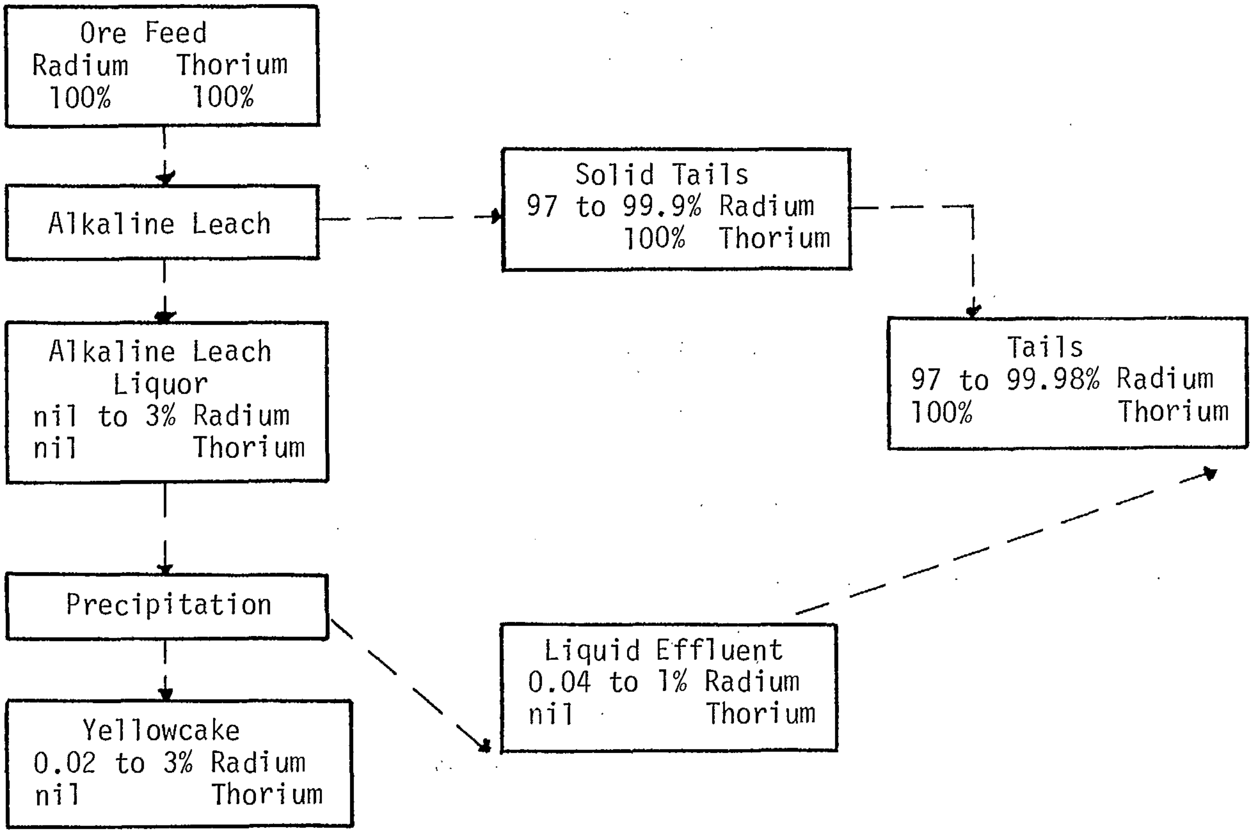


FIGURE 12

SUMMARY OF RADIUM AND THORIUM BALANCE IN ALKALINE MILL CIRCUITS

1.2.2 RADIONUCLIDE CONCENTRATIONS IN URANIUM MILLING

To assess the influences process conditions have on radium 226 exiting the plant as effluent, a summary of published data on the concentrations of radium 226 in solid and liquid process streams are presented below (see Tables 5 to 7). Detailed information is given in references 10, 10A-15, 17, 19, 20, 34.

ACID LEACH PROCESSES

1. Feed ore radium 226 varies depending on the uranium content of the ore. The radium 226 content of the ores studied varied between 360 to 680 p Ci per g dry solids. Prior to leaching, about 55% of the radium 226 is reported to be associated with the -200 mesh fraction which represents about 40% of the weight of ore (10A).

2. Sulfuric acid leaching of the ore results in a solution containing from 270 p Ci per 1 to 59,000 pCi per 1 dissolved radium depending on the flowsheet and solution recycle in the mill. Water leaching of chloride roaster product for the mill, which recovers vanadium along with uranium, gives a solution containing 4950 p Ci per 1 radium 226 compared to 1250 p Ci per 1 in the uranium acid leach liquor.

TABLE 5

SUMMARY OF RADIUM 226 CONCENTRATION IN URANIUM ACID MILL PROCESS STREAMS

Process Stream	Radium 226 Concentration (p Ci per g or l)		
Feed Ore	360	to	680
Leach Slurry			
Aqueous	270	to	59000
Solids	640	to	710
Leach Liquor to IX or SX	450	to	46400
Slurry to Tails			
Sands			
Solids	121	to	235
Liquor	114	to	1300
Slimes			
Solids	636	to	3760
Liquor	65	to	2450
Uranium Free Leach Liquor	480	to	28400
Yellowcake Product	26	to	784

TABLE 6

SUMMARY OF RADIUM 226 CONCENTRATIONS IN ALKALINE MILL PROCESS STREAMS

Process Stream	Radium 226 Concentration (p Ci per g or l)		
Feed Ore	497	to	1,103
Recycle Mill Solutions	28	to	9,560
Leach Feed			
Solids	460	to	1,090
Liquor	2,130	to	5,620
Leached Material			
Solids	207	to	1,285
Liquor	1,020	to	7,880
Liquor to Yellowcake precipitation	50	to	18,900
Yellowcake	50	to	7,190
Tailings			
Solids	190	to	1,300
Liquor	34	to	1,120

TABLE 7
SUMMARY OF RADIUM 226 CONCENTRATIONS IN URANIUM ACID MILL PROCESS STREAMS

PROCESS STREAM	RESIN IN PULP		D_2EHPA SX			CCD IX	
	A (15)	B (20)	C (11)	D (20)	E (12)	F (20)	G (10A)
Ore Feed							
U_3O_8(%)	0.2	0.324	0.21-0.49	0.27	-	0.261	-
Radium	650	878	490	874	680	769	360
Thorium	-	-	-	102	-	769	-
Leach Slurry							
Aqueous							
Radium	2,150	12,400	270	14,200	575	59,000	700
Thorium	-	-	-	-	-	-	-
Solids							
Radium	710	-	640	-	660	-	-
Thorium	-	-	-	-	-		
Leach Liquor to Uranium Recovery							
Radium	2,450	3,070	490	10,200	1,250	46,400	450
Thorium	-	-	-	-	-	-	-
Uranium Free Leach Liquor							
Radium	2,450	2,920	480	6,490	-	28,400	550
Thorium	-	-	-	-	-	-	-
Yellowcake							
Radium	150	784	35	622	26	131	330
Thorium	-	-	-	1740	-	20.2	-
Slurry to Tails							
Sands							
Solids							
Radium	170	-	235	-	140	-	121
Thorium	-	-	-	-	-	-	-
Liquor							
Radium	114	-	180	-	138	-	1300
Thorium	-	-	-	-	-		-
Slimes							
Radium	3,760	-	680	-	2200	-	636
Thorium	-	-	-	-	-	-	-
Liquor							
Radium	2,450	-	110	-	65	-	500
Thorium	-	-	-	-	-		
Tailings Pond Solution							
Radium	8* 270**	126	155	6,490	74	24,900	1675
Thorium	-	-	-	150,000	-	18,000	-
Lead	-	-	-	-	-	-	-
pH	9.5	6.8	2.1	1.8	6.9	1.8	10

Assays are quoted as p Ci per dry g residue weight or p Ci per l solution

*Sand Tailings pond solution

**Slime Tailing pond solution

Solids in the acid leach slurry prior to solid-liquid separation contain between 640 and 710 p Ci radium 226 per g dry solids.

3. Solid-liquid separation produces a leach liquor containing between 450 to 46,500 p Ci per l. Where sand-slime separation is incorporated in the solid-liquid separation unit operation the radium 226 content of the solid sands and slimes are reported as 121-235 and 636-3,760 p Ci per g respectively.

4. Extraction of uranium from the acid leach liquor by strong base anion exchange reduced the radium 226 content in one report, from 3,780 p Ci per l to 3,570 p Ci per l. No change in soluble radium was observed in the resin-in-pulp process surveyed.

   Solvent extraction with D_2EHPA is reported to reduce the radium content from 490 to 480 p Ci per l.

5. Yellowcake product is reported to contain from 26 to 784 p Ci per g radium 226.

No data are available on the concentrations of thorium 230 and lead 210 in uranium acid mill process streams.

ALKALINE LEACH PROCESSES

1. As with the acid mill circuits radium 226 is reported to concentrate in the -200 mesh ore fraction.

2. Carbonate leaching gives a pregnant liquor having a radium content varying from 2,850 p Ci per l (Beaverlodge) to 18,900 p Ci per l (U.S. Operation). Recycle of carbonate leach liquor is used in all alkaline uranium mills. In the two American mills recycle solution contained from 8,160 to 9,560 p Ci per l radium 226 (13,14). In the Beaverlodge operation, liming to control sulfate is employed and the recycle solution contains 50 p Ci per l.

3. Precipitation of the uranium with caustic gives a yellowcake containing 3,500 to 7,200 p Ci per g radium 226 (U.S. operations). In the Beaverlodge operation, prior to introducing the lime circuit, yellowcake had a radium content of 1000 p Ci per g. After the lime circuit was introduced, radium in yellowcake dropped to between 50 and 80 p Ci per g. These results indicate that radium is either adsorbed on the calcium salts or precipitated by an increase in pH in the liming circuit.

4. Liquid effluents are reported to contain from 34 to 100 p Ci per l for the U.S. operations. The data presented for the Beaverlodge operation do not make it possible to determine the level of radium in the liquid effluent.

5. Radium 226 in solid tailings vary from 490 to 510 p Ci per g (U.S. operations) and from 190 to 305 p Ci per g (+200 mesh) and 820 to 1300 p Ci per g (-200 mesh) in the Beaverlodge Operation (34).

No data are available on the disposition of lead 210 in the alkaline flowsheet.

From the above published data the following conclusions can be drawn.

- Radium 226 and thorium 230 do not follow the uranium in conventional milling practice.

- Carbonate leaching of uranium ore dissolves significantly more radium 226 than does acid leaching. Significant quantities of thorium are dissolved in acid leaching whereas minor, if any thorium is dissolved in carbonate leaching of uranium ores.

- Radium 226 dissolved in acid leaching appears to be reprecipitated or more probably adsorbed by cation exchange onto the fine clay minerals present in the slime fraction of the solid tails. In alkaline leaching the same process may be occurring.

- The processes used to recover uranium from acid leach liquors do not concentrate radium to any extent. The amount of thorium co-removed with the uranium is minimal.

- The high radium 226 levels in the solid tailings, both acid and alkaline milling, do not allow for long term surface disposal.

- Liquid effluent neutralization, or liming of carbonate barren liquors prior to recycle to the leach reduces the soluble radium 226 in excess of 90%.

- The high radium 226 content of the liquid effluent associated with the solid tailings makes treatment mandatory before discharge to natural water courses.

REMOVAL OF RADIONUCLIDES FROM PROCESS STREAMS - A REVIEW

by

I.J. Itzkovitch* and G.M. Ritcey**

CANMET REPORT 79-21

MINERALS RESEARCH PROGRAM

MINERAL SCIENCES LABORATORIES

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1.3 RADIONUCLIDES IN TAILINGS BASINS

To best evaluate practiced and proposed effluent treatment schemes, available data on the disposition of the radionuclides in tailings ponds, whether they be associated with the liquid or solid phase are presented and discussed.

Most mills discharge tailing material containing low level radioactive solids and a liquid effluent to a tailings pond. As previously stated the weight of solid tailings is approximately equal to the weight of the ore fed to the mill. These solids contain about 75% of the activity in the ore. The quantities of waste liquids produced by milling operations vary considerably depending upon the process used. Shearer (19) reported that liquid effluents produced at acid leach mills average 850 gallons per ton of ore processed, whereas for alkaline leach mills liquid effluent averaged 250 gallons per ton. Ranges for liquid effluents for acid and alkaline leach mills were given as 538 to 1,210 gallons per ton respectively. Data presented in James F. McLaren's environmental assessment of the proposed Elliot Lake uranium mines expansion gives figures for liquid effluent to tailings of 363 gallons per ton ore processed at the Denison Mill and 764 gallons per ton at the Quirke Mill (6).

These liquid mill effluents, although containing only a minor per centage of the total activity in the ore, are for the Canadian situation, the major environmental concern because tailings effluent is discharged to natural watercourses.

In the preceeding section of this report, data were given on radium 226 concentrations in mill effluents published with respect to the distribution of radium in the mill process streams. Other data have been published both with regard to liquid effluent analyses and the distribution of radium and thorium in tailings ponds. In addition, a substantial amount of data has been published on the leachability of these radionuclides. The latter is of prime importance when assessing current and proposed effluent treatment processes as they relate to life of mill and post shut-down control of radionuclide contamination.

Radionuclides in Solid Mill Tailings

Spent ore solids are an important source of environmental contamination by mill wastes. These tailing solids contain the bulk of radium 226 that enters the mill in the ore. In addition, for neutralized tailings the bulk of the thorium in the ore reports as solids to tailings. Presumably the bulk of the lead 210 in the ore also reports as solids to tailings, either because it is not dissolved in the mill process or is precipitated as lead sulfate in an acid leach mill. Ryon (35a), for six unspecified uranium mills, reported that solid tailings had a radionuclide content of 237 to 716 p Ci per g radium 226, 88 to 604 p Ci per g thorium 230, 100 to 406 p Ci per g lead 210 and 100 to 395 p Ci per g polonium 210. The median levels of radium 226, thorium 230, lead 210 and polonium 210 were calculated as 635, 314, 226, 225 p Ci per g solid respectively.

Much of what has been published with respect to radionuclide distribution and stability in solid tailings is related to radium 226.

Radium is not uniformly distributed throughout the solid tailings. It is reported to concentrate, along with its radioactive daughters, in the slimes fraction of the leach tails. About 77 to 94% of the radium 226 reports in the -150 mesh solid tailing fraction (36). Seeley (37) reported that for actual in-plant tailings, 80 to 90% of the radium is contained in the -400 mesh fractions. These fine fractions comprise 20 to 33% of the weight of acid leach process tailings and 12 to 50% of the alkaline leach tailings (38).

Radium 226 concentrations in the -20 to +140 mesh tailings fraction were reported as 50 to 400 p Ci per g whereas for slimes the radium content varied up to a reported 2300 p Ci per g depending on the mesh fraction analyzed. Moffett et al. (39) reports that in Elliot Lake acid mill tails some of the radium 226 is adsorbed on a jarosite type carrier, to a level of 80,000 p Ci per g.

Since radium is concentrated in the finest fraction of solid tailings adequate clarification of discharged liquid effluent is required to ensure that the natural watercourses remain uncontaminated. To meet the proposed AECB target of 10 p Ci per l total radium, a maximum slime content of liquid tailings effluent of 5 ppm must be ensured (assumed 2000 p Ci per g radium 226 in slimes).

From the standpoint of long-term maintenance of tailings, especially after the mill has been shut down the dissolution by leaching of radium 226 is potentially the most significant factor in ensuring minimum environmental impact by the uranium mills.

Extensive studies have been carried out in an attempt to characterize the transport of radium from uranium mill tailings piles to the surrounding environment. Shearer (40,41) conducted laboratory leaching tests on both uranium mill solids and river bottom sediments from several locations in the Colorado plateau area of the United States. A summary of his findings is given below:

Radium 226 dissolution was found to be more likely for uranium solid tailings than for ore.

In leaching radium from mill tailings and river sediments diffusion was shown to be insignificant. Essentially all of the radium that could be solubilized was leached in about 15 minutes. Grind, temperature and agitation rate had little, if any effect on the total quantity of radium dissolved whereas solid-liquid ratio and inorganic salts significantly affected the degree of radium leached.

Three distinct leaching regions were obtained for tests carried out at varying solid-liquid ratios. At high solids, decreasing the amount of solids, resulted in no change in radium dissolution. A second region existed where a small decrease in the percent solids resulted in a large increase in radium leached. Finally, a third region exists where a large decrease in the solids did not cause a marked increase in leached radium. These results, coupled with the observation that the effect of solid-liquid ratio is more pronounced for acid leach tailings than for alkaline leach process tailings, indicate that at high solids content, dissolution and re-precipitation of radium as a sulfate is occurring.

Leaching of river sediments with inorganic salt solutions showed that the order for radium dissolution was, $BaCl_2 >> SrCl_2 >> CaCl_2 > HCl > KCl > NaCl \sim MgCl_2 \sim H_2O$. A linear relationship between the amount of radium leached and barium chloride concentration was observed. These results could be explained by the displacement of radium on the sediments by the leaching cation.

Havilik (42,43) studied the leachability of radium 226 from solid mill tailings, river sediments and ore as a function of pH, salt type and concentration. His results show that radium dissolution reached a maximum in 15 to 30 minutes and then decreased with increasing time. Comparing radium dissolution from tailings and ore, it was reported that a greater amount of radium (about 10 times) was liberated from tailings compared to ore. This appears to indicate that for radium, a dissolution - reprecipitation or adsorption mechanism is in effect during milling. For both tailings and sediments radium dissolution was reported to be a maximum at pH 1, decreasing to pH 9 and again increasing to pH 13. The order of radium dissolution as a function of salt type for both tailings and ore was $BaCl_2 > K_3PO_4 > MgCO_3 > Na_3\ PO_4 > SrCl_2 > (NH_4)_2SO_4 > CaCl_2 > NaCl > KI$.

Others have also conducted laboratory studies on the leachability of radium 226 from both acid and alkaline tailings.

Wiles (44) proposed a rapid adsorption followed by a solid state interchange between barium on the surface and radium in tailings to explain his leaching data.

Levins et. al. (45) reported on leaching radium from acid process tailings with concentrated brine solutions. Radium dissolution was again shown to be inhibited by sulfate. To achieve greater than 90% radium extraction, four stage co-current leaching with 5 M sodium chloride at a solid-liquid ratio of 0.2 was required. Thorium 230 was not leached to any significant extent. No data were presented on radium recovery from the brine leach liquor but it is claimed that precipitation of barium radium sulfate or ion exchange is feasible. The effectiveness of radium recovery is stated to be reduced at high salt concentrations.

Seeley (37) reported on radium recovery from uranium mill slime tailings solids and ore by leaching with complexing agents, metal chloride salt solutions and hydrochloric acid.

Single stage leaching of slime solids at 3% solids showed that strong radium complexing agents, such as EDTA and DTPA, are effective in dissolving radium. Of the metal chloride salt solutions (1M) evaluated ferric chloride, calcium chloride and barium chloride dissolved 59, 73 and 65% of the radium respectively. Hydrochloric acid, sodium chloride and aluminum chloride dissolved 36, 36 and 20% respectively. The other metal chloride salts dissolved only about as much radium as water.

Sulfuric acid process slime tails subjected to 4 stage counter-current leaching at 3% solids with 1M NaCl - 0.1M HCl solution removed 94% of the radium. Recycle of the leach solution resulted in a decrease in radium recovery. After 8 recycles, radium dissolution was only 72%.

Presumably this decrease is due to the build-up of sulfate in the recycle chloride liquor and subsequent decrease in radium solubility.

Small scale experiments have shown that approximately one-third of the radium could be leached from Elliot Lake tailings by KCl; chlorides of other cations, such as sodium, ammonium, calcium and lithium were able to remove less than 10% of the radium (37A). A pre-wash with water followed by a KCl leach resulted in the removal of two-thirds of the radium.

All of the above studies indicate that upon discharge of uranium mill waste solids into watercourses, immediate leaching of some radium will occur. Because of the high sulfate content of many river waters a large part of the radium will reprecipitate. Of that left in solution a large part will be adsorbed onto the river sediment or the mill solids. Thus only a small amount of the radium should remain as soluble radium 226 in the natural watercourse.

The above data were obtained by agitation leaching of solid mill tailings. Of importance in the Canadian context, where precipitation exceeds evaporation, is the percolation leaching of radionuclides as it relates to abandoned tailings.

The seepage from abandoned tailings appear to represent a potential major environmental impact on natural watercourses which will require treatment for radionuclide control even after the mine mill complex has been shut down. Lysimeter studies carried out by Schmidtke et. al. (46) at water flowrates of 41 to 82 mm per month, 10 day intervals, gave effluent radium 226, lead 210 and thorium 230 in the range 62 to 81, 860 to 1100 and 245 to 1565 p Ci respectively. Simulated lime additions to the top of the lysimeter gave leachates similar to the above. Higher application rates, 460 mm per month continuous, gave levels in the range 5 to 20 p Ci per 1 radium 226, 970 and 3040 p Ci per 1 lead 210 and 68 to 693 p Ci per 1 thorium 230. Presumably the lower concentrations at the higher application rates are directly related to dilution effects. Freshly milled tailings gave seepage levels of radium 226, lead 210 and thorium 230 of 67 to 180 p Ci per 1, <15 p Ci per 1 and <50 p Ci per 1 respectively.

However, lysimeter studies on Elliot Lake tailings conducted at CANMET over a period of more than one year (simulated 7 years) show that radium but not thorium nor uranium is leached continuously (46A).

CANMET carrying out field investigations on 17 year old tailings at the Nordic tailings basin in Elliot Lake, Ontario reported levels of radionuclides in water beneath the sands and slimes as well as seepage water which in the most part, exceeds the MPCW (39). These data show that treatment of tailings pile seepage would be required after the mill was de-commissioned.

The results are summarized below:

	p Ci per 1		
Sample Location	Radium 226	Thorium 230	Lead 210
Beneath Sands	27	16,000	4,067
Beneath Slimes	137	-	42
Seepage	13	800	32
MPCW	10	2,000	100

It is important to note that the acidity of seepage water and that beneath the sands exceeded that beneath the slimes significantly.

Soluble Radionuclides

The National Lead Company (20), have reported a substantial amount of data on soluble radium in uranium mill tailings solutions for different milling processes. A limited amount of data is presented on thorium in these tailing solutions. Unfortunately, factors that would affect the radium levels in the tailings effluent, such as, dilution, recycle of tailings water, radium content of the ore, acidity etc. were not included in the report. Thus, trends in the radium level according to process could not be established. The published data are given in Table 8 and are reviewed according to the process used in the mill.

ACID LEACH - RESIN IN PULP, mill effluents (pH range 1.8 to 2.5) are reported to contain from 2,630 to 11,300 p Ci per 1 radium with the median being 6,279 p Ci per 1. For a mill effluent initially at pH 1.9, lime neutralization to pH 3.3 reduced the radium level from 8,870 p Ci per 1 to 5,320 p Ci per 1. Effluent at pH 6.7 - 7.7 gave reported radium levels of 88 - 440 p Ci per 1. The median being 244 p Ci per liter. Thorium in the acid effluents, pH 2.5, varied from 1150 to 147,000 p Ci per 1 whereas the one effluent reported at pH 6.7 had a soluble thorium content of 10 p Ci per 1. The median thorium levels were 68,750 and 10 p Ci per 1 in the acid and neutral effluents respectively.

ACID LEACH - SOLVENT EXTRACTION, with presumably D2EHPA as the extractant, gave mill effluents varying in radium content from 447 to 11,300 p Ci per 1, with the medium varying from a low of 447 to a high of 5984 p Ci per 1 depending on pH. The thorium levels varied from 130 p Ci per 1 to 5,241 p Ci per 1. Again the low levels were observed for those tailings high in pH.

ACID LEACH RESIN-IN-PULP ION EXCHANGE, tailings solution gave radium and thorium levels varying from 88 to 11,300 p Ci per 1 and 10 to 147,000 p Ci per 1 respectively. The low levels were reported for those tailings high in pH.

TABLE 8

ANALYSIS OF PUBLISHED DATA
ON TAILINGS POND RADIUM AND THORIUM

Process	Effluent pH Range	Radium in Effluent (p Ci/l) Highest	Average	Lowest	Thorium in Effluent (p Ci/l) Highest	Average	Lowest
Acid-RIP	1.6-3.3	11,300	6,279	2,630	147,000	68,750	1,150
	6.7-7.7	440	244	88	10	10	10
Acid-SX	1.5-2.0	11,300	5,984	4,010	-	-	-
	2.6-3.5	1,860	1,045	608	5,241	-	410
	6.9	447	447	447	130	130	130
Acid-IX	1.8-1.9	81,600	53,250	24,900	477,000	331,500	186,000
	3.7-7.8	820	406	32	640	337	100
Alkaline Filtration	6.7-7.1	440	218	88	10	10	10
Alkaline - RIP	10.1	113	113	113	-	-	-

ACID LEACH - CCD - ION EXCHANGE tailings solution gave radium and thorium levels varying from 32 to 81,600 p Ci per l and 270 to 477,000 p Ci per l respectively. The low levels were quoted for those tailings high in pH.

ALKALINE LEACHING gave much lower reported radium levels in the mill tailings solution. Levels of 17 to 4,910 p Ci per liter are reported. Neutralized leach mill effluents from Canadian Operations are reported to contain from 10 to 750 p Ci per l (6, 21, 22). Other data have been published but since the concentration ranges for radium and thorium are the same as above they are not discussed (5, 23 - 32).

From the above it appears that neutralization of acid tailings significantly reduces both the radium and thorium levels in the mill effluents. Thorium is reduced by hydrolysis and presumably the radium level is reduced by adsorption and/or ismorphous precipitation with calcium sulfate. It is important to note that in no case was neutralization of tailings adequate in reducing the level of radium 226 in tailings to below either the 10 p Ci per l Federal Standard or the proposed 3 p Ci per l Provincial Guideline for soluble radium 226.

FOR LEAD 210 IN TAILINGS only a limited amount of information is available.

A report issued in 1974 by the Robert S. Kerr Environmental Research Laboratory (5) presents data on effluent monitoring carried out for five uranium mills located in the Colorado River Basin over several years. The data include analyses for radium 226, lead 210, polonium 210, thorium 230 as well as uranium, gross alpha and beta in acid mill effluents. No process information, or effluent treatment procedures are given, making an analysis of the data difficult.

The data are synopsized in Table 9 and summarized below:

Effluents from the five monitored mills varied in median radionuclide concentrations from 11 to 35 p Ci per l radium 226, 7 to 621 p Ci per l lead 210 and 39 to 99,100 p Ci per l thorium 230. From the data presented none of the mills appear to practice effective radium 226 control. In addition, three of the five mills on an average exceeded the MPCW for lead 210 (33 p Ci per l).

The high concentrations of lead 210 in the monitored effluents indicate that the potential hazard due to lead 210 may equal those of radium 226.

Calculations were carried out to determine the ratios of lead 210 to both radium and thorium in the mill effluents. The ratios (Table 9) varied substantially for each of the mills. The lead

TABLE 9

COLORADO RIVER BASIN

EFFLUENT ANALYSIS

Mill Effluent No.	Effluent Radium 226 (p Ci per l)			Effluent Lead 210 (p Ci per l)			Effluent Thorium 230 (p Ci per l)			Ratio Lead 210/ Radium 226			Ratio Thorium 230/Radium 226		
	Highest	Median	Lowest	Highest	Median	Lowest	Highest	Median	Lowest	Highest	Median	Lowest	Highest	Median	Lowest
1	23.2	14	7.5	1250	621	2	300	49	3.3	116	46	0.2	14.3	3.6	0.3
2	65	28	1	53	10	0	3680	583	1.2	0.8	0.3	0.0	245	26	0.1
3	40	20	4.4	170	66	5.5	135,000	99,100	76,000	8.2	3.1	0.1	25,227	7,958	2125
4	31	11	0.5	110	39	0.7	28,000	5,011	0	44	8	0.1	8,750	1,765	0.0
5	65	35	25	20	7	0.7	69	39	3.0	0.5	0.2	0.0	2.5	1.1	0.1

210 to radium 226 ratio ranged from 0.2 to 46 with a median of 11.5 and the thorium 230 to radium 226 ratio ranged from 1.1 to 7,958 with a median of 1951.

These calcualted ratios for lead 210 to radium 226 differ from those reported by Tsivoglou and O'Connell (24) where in effluents studied for five uranium mills, possibly different from those discussed above, the ratio varied from 0.2 to 9.2 with the median being 2.5.

Assuming the original ore to be in secular equilibrium the ratio of lead to radium 226 in the effluent should be 0.014 if the lead followed the radium in the acid leach process. The reported median ratios indicate that lead 210 may be more soluble in tailings effluent than the radium. This is in agreement with published values for the solubility products of their respective sulfates; Ksp $RaSO_4 = 6 \times 10^{-8}$, Ksp $PbSO_4 = 1.4 \times 10^{-4}$ (33).

<u>Additional studies are required to determine the distribution of lead 210 in uranium mill circuits. Tailings effluents should be analyzed regularly to ensure that the MPCW is not exceeded.</u>

Analyzing the data presented with regards to radionuclides in the liquid and solid tailings of uranium mills it can be concluded that:

- Care must be taken to ensure that no tailings slimes are discharged along with liquid effluent if the AECB target of 10 p Ci per l total radium is to be achieved.

- Neutralization of liquid tailings effluents although significantly reducing the radium 226 concentration, does not reduce the level below the maximum permissible concentration.

- Limited data indicate that the maximum permissible concentration of lead 210 in liquid tailings effluent is exceeded. Monitoring of tailings effluent for lead 210 should be required.

- After the mill is shutdown, liquid effluent, seepage and run-off will have to be monitored and treated to meet the maximum permissible concentrations of radium 226, thorium 230, and lead 210.

1.4 CONTROL OF RADIONUCLIDES IN TAILINGS EFFLUENTS

Radium 226, very early on, was identified as the major isotope of concern for environmental control of liquid discharges from uranium mills. Therefore, the majority of the reported studies, even to this day, are concerned with control of this nuclide. Moreover, since acid leaching is by far a more widely used processing technique, studies for acid mill effluent control far exceed those reported for alkaline mills.

The average radium 226 concentration in fresh water across the U.S.A. is reported to be 0.04 p Ci per l (47). Tsivoglou (24) reported that the background concentration of dissolved radium 226 in Western United States surface waters are, for the majority, less than 0.1 p Ci per l with a small fraction of results giving concentrations in the range 0.2 to 0.3 p Ci per l. Lead 210 was less than 0.1 to 0.2 p Ci per l background. River sediments contained 1.3 p Ci radium 226 per g dry sediment as background.

In contrast, the Animas River study carried out in 1958 to 1959 showed average dissolved radium 226 concentrations of 13 p Ci per l with some samples as high as 88 p Ci per l (24). The Animas River muds analyzed as high as 800 p Ci per g radium 226.

These early studies led to industry-wide measures to minimize pollution by the uranium milling industry, both in the U.S.A. and Canada. For those mills discharging effluent to the rivers, these measures included tailings neutralization and impoundment for solids discharge control as well as precipitation of residual radium 226 as $BaRaSO_4$ by the current accepted practice of controlled barium chloride addition. Several mills use evaporation ponds to dispose of waste liquids. The Anaconda Company, of Grants, New Mexico, has used deep well injection for liquid effluent disposal (26). Table 10 synopsizes tailings disposal and treatment methods practised in the Western World Uranium mills (6).

In 1963 Tsivoglou reported (24) that since introducing control measures the dissolved radium 226 level in the Animas River was reduced to below 1 p Ci per l and river sediments, with the exception of three locations, were now at background.

The removal of soluble radium from neutralized tailings effluent was first practised commercially in the period 1958 to 1960 at Union Carbide's Uravan, Colorado uranium mill (26). The radium decontamination circuit utilized natural barium sulfate, barite.

In Elliot Lake, Ontario the addition of barium chloride to all operating and some non-operating tailings basin effluents was initiated in 1965. Prior to barium chloride treatment Yourt (48) reported radium 226 effluent concentrations of 215 p Ci per l. Addition of barium chloride to neutralized tailings

TABLE 10

WESTERN WORLD URANIUM MILLING PLANTS TAILINGS TREATMENT AND DISPOSAL METHODS (6)

Company	Mill Location	DISPOSAL METHODS		TAILINGS TREATMENT	
		Solids	Liquids	pH Control	Radium Control
CANADA					
Agnew Lake Mines Ltd. (1)	Espanola, Ontario	None	decant	yes	yes
Denison Mines Ltd.	Elliot Lake, Ontario	Drainage basin	decant	yes	yes
Eldorado Nuclear Ltd. (2,3)	Beaverlodge, Saskatchewan	Under water	decant	no	yes
Madawaska Mines Ltd.	Bancroft, Ontario	Dry land	seepage	yes	yes
Gulf Minerals Canada Ltd.	Rabbit Lake, Saskatchewan	Drainage basin	decant	yes	yes
Rio Algom Limited	Elliot Lake, Ontario	Drainage basin	decant	yes	yes
UNITED STATES OF AMERICA					
The Anaconda Company	Grants, New Mexico	Dry land	evaporation	no	no
Atlantic Richfield Co. (4)	Clay West, Texas	None	evaporation	no	no
Atlas Corporation	Moab, Utah	Dry land	decant	no	yes
Continental Oil Co.	Falls City, Texas	Dry land	evaporation	no	no
Cotter Corporation	Canon City, Colorado	Dry land	evaporation	no	no
Dawn Mining Co.	Ford, Washington	Drainage basin	evaporation	no	no
Exxon Company, USA	Powder River, Wyoming	Drainage basin	evaporation	no	no
Federal American Partners	Gas Hills, Wyoming	Dry land	evaporation	no	no
Kerr McGee Corporation	Grants, New Mexico	Dry land	evaporation	no	yes

TABLE 10 (Cont'd.)

		DISPOSAL METHODS		TAILINGS TREATMENT	
Company	Mill Location	Solids	Liquids	pH Control	Radium Control
UNITED STATES OF AMERICA (Cont'd.)					
Petrotomics Company	Shirley Basin, Wyoming	Dry land	evaporation	no	no
Rio Algom Corporation(5)	Moab, Utah	Dry land	evaporation	no	no
Sohio Petroleum Company	Laguna, New Mexico	Drainage basin	evaporation	no	no
Union Carbide Corp.	Uravan, Colorado	Dry land	decant and seepage	yes	yes
Union Carbide Corp.	Gas Hills, Wyoming	Dry land	evaporation	no	no
United Nuclear Corp.(5)	Churchrock, New Mexico	Dry land	evaporation	no	no
United Nuclear - Homestake Partners	Grants, New Mexico	Dry land	evaporation	no	no
Utah International, Inc.	Gas Hills, Wyoming	Dry land	evaporation	no	no
Utah International, Inc.	Shirley Basin, Wyoming	Dry land	evaporation	no	no
Western Nuclear, Inc.	Jeffery City, Wyoming	Dry land	evaporation	no	no
Wyoming Minerals Corp.(4)	Bruni, Texas	None	evaporation	no	no
EUROPE					
S.I.M.O.	Bessines, France	Dry land	decant	yes	no
S.I.M.O.	Escarpiere, France	Dry land	decant	yes	yes
Commisariat a l'Energie Atomique(3)	Forez, France	Dry land	decant	yes	yes
A.B. Atomenergi(6)	Ranstad, Sweden	Dry land	decant	yes	no

TABLE 10 (Cont'd.)

		DISPOSAL METHODS		TAILINGS TREATMENT	
Company	Mill Location	Solids	Liquids	pH Control	Radium Control
AFRICA					
C.O.M.U.F.(9)	Mounana, Gabon	Drainage basin	evaporation	yes	no
S.O.M.I.A.R.	Arlit, Niger	Dry land	evaporation	yes	no
Anglo American Corp. of South Africa Ltd.	President Brand, South Africa	Dry land	evaporation	yes	no
Anglo American Corp. of South Africa Ltd.	Vaal Reefs, South Africa	Dry land	evaporation	yes	no
Anglo American Corp. of South Africa Ltd.	Western Deep, South Africa	Dry land	evaporation	yes	no
Anglo Transvaal Consolidated Investment Co. Ltd.(8)	Hartebeestfontein, South Africa	Dry land	evaporation	yes	no
Anglo Transvaal Consolidated Investment Co. Ltd.	Loraine, South Africa	Dry land	evaporation	yes	no
Anglo Transvaal Consolidated Investment Co. Ltd.(7,8)	Virginia, South Africa	Dry land	evaporation	yes	no
General Mining and Finance Corp.(7)	Buffelsfontein, South Africa	Dry land	evaporation	yes	no
General Mining and Finance Corp.	West Rand, South Africa	Dry land	evaporation	yes	no
Gold Fields of South Africa Ltd.(8)	West Driefontein, South Africa	Dry land	evaporation	yes	no
Rand Mines Ltd.(7,8)	Blyvooruitzicht, South Africa	Dry land	evaporation	yes	no
Rand Mines Ltd.(7)	Harmony, South Africa	Dry land	evaporation	yes	no
Palabora Mining Co. Ltd.	Phalaborwa, South Africa	Drainage basin	evaporation	-	-

TABLE 10 (Cont'd.)

Company	Mill Location	DISPOSAL METHODS		TAILINGS TREATMENT	
		Solids	Liquids	pH Control	Radium Control
AFRICA (Cont'd.)					
Rossing Uranium Ltd.	Swakopmund, South West Africa	Drainage basin	evaporation	no	no
<u>AUSTRALIA</u>					
Mary Kathleen Uranium Ltd.	Mary Kathleen, Queensland	Drainage basin	evaporation	no	no

<u>COMMENTS</u>:

(1) Some ore is mined for leaching in heaps on surface.

(2) Pyrite floated but discharged with the other tailings solids.

(3) Some tailings used as mine backfill.

(4) Solution mining only.

(5) Mine water treated for radium control before separate disposal.

(6) Chlorine added before decanting to oxidize Mn.

(7) Pyrite recovered for acid manufacture.

(8) Uranium tailings sent to gold recovery mill.

(9) Will use the open pit for future disposal of tailings.

slurry prior to discharge to the tailings pond reduced the radium 226 level in the effluent to about 150 p Ci per l whereas when added to clear tailings decant the radium level dropped to a reported 3 p Ci per l. Current practice for operating tailings areas is to add barium chloride at a rate of 0.1 to 0.22 lbs per 1000 U.S. gal. of decant treated. The barium radium sulfate precipitate, being very fine, is settled in another settling basin, the decant of which is discharged to the natural watercourses (6). Claimed reduction in soluble radium 226 is from an initial level of 350 to 1000 p Ci per l in the tailings decant, to a level of 2 to 7 p Ci per l in the $BaRaSO_4$ settling basin decant for the Denison Mill and from 400 to 1000 p Ci per l to 3 to 10 p Ci per l for the Quirke Mill (6). For the alkaline circuit at Eldorado Nuclear Limited, Beaverlodge Operation tailings decant is reported to contain 68.5 p Ci per l dissolved radium 226. Addition of barium chloride and settling of the precipitated $BaRaSO_4$ gives an overflow of 3.6 p Ci per l (49). None of the operations claim consistent reduction to the 3 p Ci per l, Ontario or Saskatchewan, Ministry of Environment, effluent objectives.

What follows is a review of the studies leading to the presently-accepted treatment methods for control of radionuclides in tailings effluents discharged to natural watercourses. Recent test programs being carried out to meet the Provinces of Ontario and Saskatchewan objective of 3 p Ci per l soluble radium 226 and AECB target of 10 p Ci per l total radium 226 are also reviewed.

NEUTRALIZATION OF ACID MILL EFFLUENTS

Early studies at National Lead Co. Inc., Winchester Laboratory showed the advantage of neutralizing acidic mill effluent for control of dissolved radium and thorium. For effluent at pH 2, neutralization to pH 9 with lime, ammonia or caustic was shown to reduce the soluble radium 226 concentration by 97, 93 and 98% respectively. Residual soluble radium 226 was in the range, 94 to 250 p Ci per l, thus still exceeding the MPCW (28). Lime was preferred as a neutralizing agent as it was the most effective and economical (28). Soluble thorium was easily reduced to below the specifications for the mill effluents by neutralization to a pH of 5.0 or higher (20). Thus, although neutralization is effective in reducing soluble thorium to levels which meet discharge requirements, further treatment is required to reduce soluble radium to acceptable levels.

Technically acceptable procedures, which over the years have proved effective for dissolved radium removal, include adsorption onto barite (crude barium sulfate) (28), addition of freshly precipitated barium sulfate (27) or barium chloride to neutralized acid mill effluents (27). Similar radium carriers were shown to be effective for alkaline leach mill liquid effluents when sulfate in the form of copperas ($FeSO_4.7H_2O$), sulfuric acid or alum was used in conjunction with the barium salt or barite (28,20).

Other adsorbents or precipitants, bentonite, humic acid, vermiculite and lead nitrate (28), have been screened for radium and thorium removal from acid mill effluents. They were found to be either ineffective or, in the case of lead, a potential pollutant in their own right.

Barite Treatment

Contact of radium-bearing uranium mill tailings effluent with natural barium sulfate, or barite, provides a specific process for removing radium. The mechanism by which radium is removed from solution is unclear. Presumably radium is first adsorbed on the barite surface, by exchange with the barium ions on the surface. Radium is then slowly incorporated into the crystal lattice during recrystallization of the solid (20).

Detailed laboratory and pilot plant data show the utility of barite in reducing the level of soluble radium by up to 99.8%. Final effluents with a radium 226 content of below 6 p Ci per l could be obtained (28).

Misawa et al. (25) reporting on the passing neutralized acid mill tailings effluent through a column containing barite showed that the soluble radium level could be reduced from an initial 110 p Ci per l to 3.4 p Ci per l at a flowrate of 3.8 USGPM per ft^2.

Reducing the flowrate of effluent to the barite column gave final effluent radiums of 1.0 p Ci per 1 and less (See Table 11).

Pilot plant studies on un-neutralized acid mill effluents carried out by Winchester Laboratories (20) showed that, for downflow adsorption of radium onto barite at a flowrate of 1.33 USGPM per ft^2, the soluble radium could be reduced from an average initial level of 384 p Ci per 1 to an average 3.7 p Ci per 1, range 0 to 5 p Ci per 1, for 10,000 bed volumes of effluent treated. Barite consumptions were reported to be 4.15 lbs per U.S. gal. of treated effluent. Increasing the number of bed volumes to 14,000 decreased the barite consumption to 2.74 lbs. per 1000 U.S. gal treated and increased the average radium in the final effluent to 5.9 p Ci per 1, range 0.5 to 15 p Ci per 1. Operating difficulties included slime build-up on the top of the barite bed necessitating a constant removal of the top 1 to 1.5 inches of the bed. Reported increase in head pressure required to maintain a flowrate of 1.33 USGPM per ft^2 was 0.8 ft. water per hr.

Perez et. al. (50) reporting on operations at Andujar Uranium mill states that passing tailings pond effluent through a barite bed gave erratic results for radium removal. Decontaminations of the order of 75% were occasionally achieved.

TABLE 11

EFFECT OF FLOWRATE AND BARITE PARTICLE SIZE ON RADIUM DECONTAMINATION OF NEUTRALIZED ACID MILL WASTES (25)

	Feed Ra	Flowrate USG per min per ft^2	Ra in Column Effluent p Ci per l
-10 + 32	110 p Ci/l	0.1	0.2
		0.2	0.3
		0.4	0.4
		1.2	1.0
-32 + 65	110 p Ci/l	0.2	0.3
		0.4	0.6
		1.2	1.0
		3.8	3.4

Pilot plant studies carried out on radium removal from alkaline mill effluents, using barite, showed a reduction in final effluent radium to a level of 2 to 13 p Ci per 1 depending on the treatment procedure employed (20, 28). Copperas ($FeSO_4.7H_2O$) and sulfuric acid were used as a source of sulfate. In all cases batch treatment was employed. The results summarized in Table 18 show the utility of allowing sufficient settling time between the copperas and barite treatment stages. In addition, they show that precipitation of radium by sulfate addition to alkaline mill effluent is not sufficient to reduce the radium level to below 10 p Ci per 1.

Summarized below are the factors which have been shown to influence radium removal from tailings effluents by barite treatment. For ACID MILL EFFLUENTS, these factors include,

1. Temperature - radium removal from neutralized acid mill effluents improved with increasing temperature indicating an adsorption mechanism (27).

2. pH - maximum removal of radium is achieved at pH 8 (27).

3. Barite Mesh Size - in batch contacts, mesh size was shown to influence the rate of radium uptake (20), whereas in column operation the size range of the barite showed little influence. (25).

4. Type of Contact - countercurrent batch and column contact was shown to be more efficient than co-current batch contact (23).

5. Contact Time - for batch contact, radium adsorption was initially rapid. Continued adsorption of radium was proportional to contact time (28).

6. Organic Impurities in Effluent - soluble organic from D_2EHPA uranium recovery circuits in the tailings effluent inhibited radium adsorption onto barite (51).

7. Column Influent Flowrate - Increasing the flowrate of tailings pond effluent to the barite column gave increasing radium in the final effluent (25).

For ALKALINE MILL EFFLUENTS factors included:

1. Slime Removal Prior to Sulfate Addition - improved radium removal by a factor of five. Flocculants tested showed slime removal best with separan or alum (28).

2. Source of Sulfate - sulfuric acid or ferrous sulfate gave effective radium removal (20,28).

3. pH - maximum radium removal observed at pH 8 (27).

4. Type of Contact - countercurrent or column adsorption of radium is indicated to be more efficient than successive batch contact yet the latter was used in the pilot plant studies carried out at the Monticello Mill (28).

In-Situ Radium Precipitation

Following extensive laboratory studies, carried out in the late 1950's and early 1960's, it was found that in-situ precipitation of barium radium sulfate by the addition of barium chloride or barium carbonate to tailings effluent was more efficient and economical than barite alone for soluble radium removal. A new radium decontamination circuit was installed at the Union Carbide Uravan Mill in 1960 (26). The process, which has become accepted practice today, involves adding a concentrated solution of barium chloride to clarified effluent. Radium is coprecipitated with insoluble barium sulfate formed by the reaction of barium with solution sulfate. The fine precipitation is settled before the effluent is released to the environment.

The results of mill-scale decontamination studies on the effectiveness of different barium compounds in reducing the level of soluble radium in neutral uranium-vanadium plant effluent and acidic effluent (pH 2.0) are given in Table 12 (26). Each pilot study lasted from one week to one month or more to ensure stable operating conditions.

TABLE 12

RADIUM DECONTAMINATION USING BARIUM SALTS. MILL SCALE TESTS AT UNION CARBIDE'S URAVAN, COLORADO MILL (26)

Effluent	Reagent	Reagent Addition (g/l)	Radium Concentration (pCi/l) Before Treatment	Radium Concentration (pCi/l) After Treatment	Radium Removal (8)
Neutral	$BaSO_4$	0.3	100	30	70
		1.0	300	70	77
	$BaCO_3$	0.1	470	30	94
		0.2	490	40	92
	$BaCl_2$	0.03	800	20	97
		0.06	440	6	99
		0.1	400	2	99
		0.2	430	2	99
Acidic	$BaCO_3$	0.1	150[1]	18[2]	88[2]
		0.2	150[1]	20[2]	87[2]
		0.3	150[1]	30[2]	80[2]
	$BaCl_2$	0.1	150[1]	5-15	90-97

[1] Based on average of several sampling periods; individual samples were somewhat erratic.

[2] Difference in results not considered significant.

In most cases it was found the barium added as a chloride was more efficient than the carbonate or sulfate salts. Radium in the final effluent, discharged to natural watercourses was below 10 p Ci per l.

Barium as a carrier for radium was first used in 1898 by Pierre and Marie Curie to isolate a new radioactive substance, namely radium (52). Commercially, barium was used to recover radium from pitchblende concentrates in the 1930's at Port Hope Ontario (53). Numerous laboratory, pilot plant and mill studies have been carried out since the rediscovery of the utility of using a barium salt to reduce the radium level in uranium mill tailings discharge.

Feldman (27), reviewing the studies carried out by the Winchester Laboratories during the period 1959 to 1961, cited the following factors as influencing radium removal from acid mill tailings effluents. Other researchers have verified these results in subsequent test programs over the intervening years.

1. <u>Barium Sulfate vs. Barium Chloride</u> - radium removal by in-situ precipitation of barium sulfate is more efficient than adsorption on the same amount of preformed barium sulfate.

   Levels of residual radium using barium chloride were about 50% lower than those obtained when barium sulfate was used. Chardon (30) showed that whereas

10 mg per l barium chloride (9.5 mg per l barium sulfate equivalent) gave a final effluent containing 4 p Ci per l radium, 500 mg per l of pre-precipitated barium sulfate was required to give the same soluble radium.

2. Suspended Solids - radium removal efficiency increased with decreasing suspended solids in the effluent.

Addition of 10 mg. per l barium chloride to filtered acidic effluent reduced the soluble radium from 370 p Ci per l to 41 p Ci per l compared to a reduction to 96 p Ci per l when the effluent was not filtered. Yourt (48) reported the same observation when the barium chloride was added to Rio Algom tailings pond as compared to the tailings decant. Levels of soluble radium were about 150 p Ci per l in the former and below 10 p Ci per l for the latter addition mode. Chardon (30) showed that to achieve a 10 p Ci per l soluble radium in final effluent less than 10 mg per l barium chloride was required for clarified effluent compared to 2 gpl barium chloride when the effluent was not clarified.

3. Barium Chloride Concentration - soluble radium removal was found to be linearly dependent on the concentration of barium chloride added.

Doubling the barium chloride addition reduced the radium level in the final effluent by one-half up to a lower limit of soluble radium (20 p Ci per 1) after which increasing the barium chloride addition had marginal effect on radium solution. For an initial radium solution of 500 p Ci per 1 Chardon reported that adding 10 mg of barium chloride per 1 of clarified effluent reduced the radium to 4 p Ci per 1. (30)

4. <u>Initial Radium In Effluent</u> - the quantity of barium chloride required was shown to be dependent on the initial radium in solution. Results showed radium removal to be more efficient at low initial radium concentrations.

5. <u>pH</u> - Confilicting data are presented in the literature. Feldman stated that the initial pH of the effluent did not influence decontamination (27). In WIN-121 (51) it is reported that coprecipitation of barium radium sulfate is best carried out "slowly" at pH 3. At higher and lower pH values it is claimed that the crystal size of the precipitate is decreased and radium removal adversely affected.

6. Rate of Addition of Barium Chloride - the removal of radium from solution was found to be higher when the barium chloride solution was added very slowly. This was probably due to reduced high localized concentrations of precipitated barium sulfate which would limit the adsorption of the radium.

7. Two Stage vs. One Stage Barium Chloride Precipitation - two successive additions of barium chloride are not beneficial. The removal of radium was shown to be far below what was expected from the cummulative effect of the two cycles.

   Other data presented by Feldman show that whereas barium added to acid effluents as chloride or carbonate is effective in substantially reducing the level of soluble radium 226 (up to 90%) only about 60% of the radium 223 is precipitated.

Lakshmanan et. al. reported that soluble radium in Eldorado's Beaverlodge alkaline mill is controlled in the tailings to less than 3 p Ci per l by barium chloride precipitation of barium radium sulfate (49). No other mention has been found in the literature of soluble radium control in final tailings effluents from alkaline mills by barium chloride additions.

RECENT TEST PROGRAMS

Although it is generally accepted that addition of barium chloride to tailings pond effluent will, if operated properly, reduce soluble radium 226 to below 10 p Ci per l two potential difficulties remain. Namely, assurance that the precipitated barium radium sulfate is not discharged as a solid to natural watercourses and secondly the question of long term stability of impounded barium radium sulfate.

Contamination of receiving waters by suspended barium radium sulfate will result in an increase in the radium content of river sediments. Subsequent leaching of this sediment by river water may result in drinking water contamination downstream from the mill. This has resulted in the AECB setting a target level of 10 p Ci per l total radium 226 in effluents discharged to natural watercourses.

If the barium radium sulfate is susceptible to natural leaching by e.g. drainage from tailings ponds or rain and snowfall, the radium could, either during mill operation or more likely once the mill with its tailings area and barium radium sulfate settling basins were decomissioned, find its way into the ecosystem.

Both of the above concerns have been addressed in the current literature.

Single stage precipitation of radium by controlled additions of barium chloride to either neutralized acid mill tailings decant or alkaline mill tailings decant to which sulfate has been added results in a fine barium radium sulfate whose settling characteristics are poor. Chardon and Kremer (30) reported initial settling rates of 0.065 m per hour for freshly precipitated barium radium sulfate. Iwata et. al. gives initial settling rates of 0.012 m per hour (54).

As shown below, currently designed settling basins do not provide sufficient retention time to meet the 10 p Ci per 1 total radium 226 target. Schmidtke et. al. (46) showed that six hour settling of precipitated barium radium sulfate reduced the total radium 226 (dissolved plus suspended) from about 1000 p Ci per 1 to about 45 p Ci per 1.

Moffett and Vivyurka (55), carrying out laboratory studies on Quirke Mill Effluent, showed that after 48 hours settling total radium 226 in the overflow was reduced from greater than 294 p Ci per 1 to 18 p Ci per 1. Analysis of the Quirke Effluent Treatment system showed that whereas barium chloride treatment reduced soluble radium 226 to below 10 p Ci per 1, total radium sulfate in the settling basin overflow had a mean of 8 6 p Ci per 1 (two stage barium chloride treatment) and 56 to 70 p Ci per 1 with a single stage treatment with barium chloride.

A number of studies have been carried out with the intent of improving the settling rate of precipitated barium radium sulfate. Much of what is reported is conflicting.

Kremer in 1968 patented the use of fatty acid salts such as sodium stearate and sodium oleate to flocculate barium radium sulfate (56). A 2.3 fold improvement in settling rate, to 1.5 m per hr., is claimed. Chardon and Kremer verified the patent claims in scale model tests at the Bois-Noirs Uranium Mill (30).

Fournier disputes the above (57). Poor results were obtained in pilot plant tests at the Bessines Uranium Mill using fatty organic acid flocculants. Improved settling was claimed using mechanical flocculation (baffles) with or without anionic flocculants (Floerger FA - 20H). Chemical flocculant was claimed to improve settling efficiency from 54% obtained with baffles alone to 75% using both baffles and flocculant.

Iwata et. al. reported that, for the Ningyo-Toge Uranium processing pilot plant, additions of bentonite improved the settling rate of barium radium sulfate from an initial 0.012 per hr. to 0.14 m per hr. (54).

Wilkenson and Cohen studying the flocculation of barium radium sulfate from acid and carbonate uranium mill effluents claimed that anionic and non-ionic polymers, ferric sulfate, commercial organic fatty acids, kaolin and bentonite clays were ineffective in promoting floc formation (58). Ferric chloride, alum or high iron acid seepage from the Elliot Lake area produced a bulky floc. Their addition to unfiltered tailings decant water resulted in <10 p Ci per l radium 226 after settling. Settling rates were reported to improve with flocculant dosage, time and speed of agitation.

Mini-plant flocculation studies, using ferric chloride hexahydrate at dosage levels of 10 and 40 mg per liter of neutralized barium chloride treated acid mill decant, indicated a reduction in total radium to below the 10 p Ci per l target given a settling time of 6 hours (46). Pilot testing of ferric chloride flocculation of barium sulfate is currently going on at Rio Algom's Quirke Mine in Elliot Lake, Ontario (35).

Full scale plant trials carried out by Rio Algom, separate to the testwork reported above, showed the utility of adding ferric chloride to the overflow from barium chloride treatment and re-settling the flocculated barium radium sulfate. (55). Addition of ferric chloride reduced the total radium 226 activity to 20 p Ci per l compared to a mean of 70 p Ci per l obtained with double settling and no ferric chloride addition. It was concluded that small doses of ferric chloride substantially reduce the total radium 226 loadings to surface watercourses.

Use of ferric chloride would substantially increase the amount of solids retained in the settling pond, thus reducing the lifetime of the settling basin making the second concern, namely the stability of barium radium sulfate of equal importance.

Early studies (51) showed that water will leach radium from barium radium sulfate. The leaching was found to be inhibited by the presence of 350 to 1420 ppm sulfate added as sodium sulfate. In the absence of sulfate, leach waters containing about 40 p Ci per l radium 226 were obtained compared to 11 to 15 per l for sulfate containing leachant.

Recently reported results on the effect of pH and sulfate on the release of radium from a synthetic barium radium sulfate sludge are erratic (39). Sulfate, as in the Winchester studies, reduced radium 226 release. Apparently, minimal release occurs at 800 ppm sulfate. The results reproduced on Table 13 indicate a strong interaction between acidity and pH on radium dissolution.

Lysimeter studies carried out by the Canadian Centre for Inland Waters on leaching of barium radium sulfate sediments showed that the average radionuclide content of water at pH 8 overflowing the sludge were 7 p Ci per l, for radium 226, less than 15 p Ci per l for lead 210 in the latter part of the test and 50 p Ci per l for thorium 230 respectively (46). Chemically fixed sediments, fixation unspecified, gave radium in the water of less than 3 p Ci per l.

Preliminary experiments reported by Ritcey (10) indicate that anaerobic sulfate reducing organisms, if established in the barium radium sulfate settling basins, would promote the dissolution of the sludge. If this occurred, not only would the radium levels exceed the 3 p Ci per l standard but toxic barium would exceed the 1 ppm standard.

TABLE 13

^{226}Ra ACTIVITY (pCi/L) IN SOLUTIONS OVERLYING SLUDGES

pH	Sulfate Concentration (ppm)			
	0	250	800	1500
2		3.0	1.2	8.2
4		5.2	1.2	6.2
6	56.8*	39.8	38.2	4.4
7		61.0	2.2	2.8
8		41.6	1.4	26.0
10		66.0	1.2	36.6

* Mean of 3 values in distilled water (pH 6.5).

From published data it is concluded that:

- Soluble thorium 230 is adequately controlled in acid mill effluents by neutralization to pH or higher. No added treatment for thorium 230 control is required for carbonate mill effluents.

- Of the options evaluated on pilot scale or employed in uranium mills for radium 226 control, precipitation of barium radium sulfate by controlled additions of barium chloride is the "Best Available Practical Technology".

- Levels of less than 3 p Ci per l soluble radium will be difficult if not impossible to achieve using barium chloride. A lower limit of 10 p Ci per l would appear realistic.

- The target level of 10 p Ci per l total radium in tailings effluent will not be attained using simple settling of barium radium sulfate. Use of flocculants appears to have promise. Discrepancies in the literature have to be resolved.

- Redissolution of precipitated barium radium sulfate poses a potential long term environmental problem. Many of the factors affecting the kinetics of redissolution need to be extensively studied.

Alternatives to barium radium sulfate precipitation as a means of controlling radium need to be developed if the provincial standard of 3 p Ci per l soluble and the AECB target of 10 p Ci per l are to be met consistently. The alternative of radium adsorption onto barite shows promise and should be re-evaluated with the view to reducing barite consumption and meeting the above limits.

SECTION II - ALTERNATE PROCESSING TECHNOLOGY FOR URANIUM MILLING

As previously shown, more than 95% of the uranium ore when processed by conventional means reports as insoluble tailings that contain little uranium but most of the original radioactivity. Mill waste typically contain 700 p Ci radium per g. of solids.

If no action were taken with respect to this radioactivity the tailings pile may be regarded as reported by Goldsmith et. al. (60) as:

- a large highly-dispersed uncontained source of radioactivity.
- an unattended source of radioactivity with minimal restraints to public access.
- a source of radioactivity that will yield continuous exposure to radiation for several thousand years.

Public access to the tailings pile would have to be controlled to prevent it from being removed by individuals for private use. This controlled containment of radium bearing tailings would be expensive and ultimately unsuccessful.

The hazards associated with the use of uranium tailings as a source of building materials or with habitation near mill tailings could be eliminated by removing the radium 226 and its parent thorium 230. Tailings could be reprocessed for radionuclide removal or more preferable, technology could be developed which, at the same time as uranium is won from the ore, the radionuclides of concern are reduced to safe levels.

Raicevic has reported on the flotation treatment of old and new tailings of Elliot Lake (60A). A concentrate was produced which comprised 20-30% by weight of the original tailing and rejected over 98% of the pyrite, 70-75% of the radium 226, about 60% of the uranium and 60-65% of the thorium. The final tails contained 0.05-0.08% sulphur as pyrite, 0.003-0.004% uranium, 0.01% thorium and 50-60 p Ci per g radium 226.

Limits for radium in building materials have been set in the United Kingdom and the U.S.S.R. and have been accepted world wide. In the United Kingdom maximum permissible content for radium of 25 P Ci per g has been recommended for gypsum wall board and buliding blocks (61). A total of 20 p Ci of radium and related nuclides per gram of building materials is permitted in the U.S.S.R. (62).

Considering the 1,600 year half life of radium, 10,000 years of controlled storage would be required to reduce the radium level in tailings from 700 p Ci per g to the 20 p Ci per g standard through natural decay. Thorium 230 in the tailings would increase the required storage time many fold, as its decay will replenish the radium 226.

Reference to processing uranium ore by alternate technology with the stated purpose of producing tailings low in radium, thorium and lead is limited. Some studies have been carried out using chloride as a metal salt or acid, nitric acid or strong complexing agents as leachants. Chlorination of uranium ore has also been evaluated. These processes are discussed below along with proposed control procedures for the radionuclides.

11.1 CHLORIDE PROCESSES

Sawyer et. al. (63) patented a process for the recovery of uranium and radium from uranium ores by ferric chloride leaching. Claimed extractions ranged from 95 to 97% for uranium and 85 to 89% for radium. To remove radium from the leach liquor sulfuric acid and a barium salt is added to precipitate barium radium sulfate. Greater than 80% recovery of radium from the leach liquor is claimed.

Borrowman and Brooks (36) studied the leaching of ore and mill tailings with EDTA and hydrochloric acid.

For acid process tailings three consecutive treatments at 60°C with 0.15 M EDTA, 15% solids or 3 consecutive leaches at 60°C with 1.5 M hydrochloric acid, 25% solids gave residues containing 40 p Ci per g radium. Following EDTA extraction, dissolved radium was reduced by 94% by acidification to pH 2.5 with sulfuric acid followed by the addition of barium chloride to reprecipitate barium radium sulfate. Further acidification of the radium free liquor, precipitates the EDTA for reuse. Chemical costs alone were reported to range from $30.00 to $50.00 per ton of tailings treated.

Leaching of the alkaline process tailings with EDTA gave poor extractions. Only 56 per cent of the radium was extracted.

Leaching of uranium ore with a combination of sulfuric acid and complexing agents, including citric acid and EDTA, proved ineffective.

Countercurrent leaching with 1.5M hydrochloric acid at 60° C, 25% solids leached more than 99% of the uranium and reduced the radium content of the leach residues to 60 and 170 p Ci per g for two different ores. The differences in final radium in the leach residues was shown to be a function of the initial sulfur content of the ore - the higher the sulfur content the less radium extracted. This inhibitory effect was related to reduced radium solubility with increased sulfate in the hydrochloric acid leach liquor. The inhibition could be reduced by increasing the quantity of hydrochloric acid used in leaching.

Uranium in the leach liquor was recovered by solvent extraction with a mixture of D_2EHPA and TOPO. Radium in the leach liquor, originally at 200,000 p Ci per l was reduced to 400 p Ci per l using 1.67 lbs barium chloride and 2.50 lbs sodium sulfate per 1000 U.S. gal. leach liquor. Assuming 2 lb U_3O_8 per ton of ore leached, treatment costs calculated for barium and sodium sulfate alone amount to 9.8 cents per lb U_3O_8 produced, excluding freight (December 4, 1978 chemical costs as reported in Chemical Marketing Reporter).

Seeley (37) showed that 3 stage co-current leaching at 85°C of Ambrosia Lake sandstone ore with 3M hydrochloric acid removes 90% of the radium in the first stage and an overall removal after the 3 stages of 94% was reported. A residue containing 37 p Ci per g radium was produced. No mention is made of possible processing of the leach liquor for radium removal.

Ritcey (10) and Haque (10B, 10C) reported on new and improved methods for the extraction of uranium from Elliot Lake, Ontario ore (50% -200 mesh) with hydrochloric acid at 60% solids. The effect of leach temperature and time, quantity of hydrochloric acid and sodium chlorate additions on the extraction of uranium, thorium and radium were determined.

The results indicated that extractions of 96% U, 81% Th, and 91% Ra^{226} could be obtained in a single stage of leaching. Using a two-stage leach, the recoveries were increased to 98% U, 83% Th, and 98% Ra^{226}. The radium content of the tailings, after two-stage leaching, is 15-25 p Ci per g. No economic assessment has yet been made, and no isolation tests for radionuclides have been carried out.

A second route (10, 63A) investigated shows good promise in reducing the environmental hazards associated with radium in the solid tailings. The process studied was dry chlorination of uranium ore followed by dilute hydrochloric acid leaching of the calcine (See Figure 13).

In this process, a portion of the uranium, thorium and iron are volatilized as chlorides during chlorination in the range 400° to 1000°C. Leaching the calcine with dilute hydrochloric acid solubilizes a large portion of the remaining uranium, iron, thorium and the radium present as chlorides. Overall extractions of uranium and radium of 90 to 95% are claimed. A final residue for disposal containing 0.02% thorium and 20-30 p Ci radium 226 per g is produced. Radium in the dilute hydrochloric acid may be precipitated as barium radium sulfate by additions of sulfuric acid and barium chloride, or isolated and concentrated by other methods.

The flowsheet is in the early stages of continuous testing. It is unknown whether or not the build-up of sulfate in the leach liquor through the addition of sulfuric acid for radium control will not, as Borrowman reported (36), inhibit the leaching of radium from calcine.

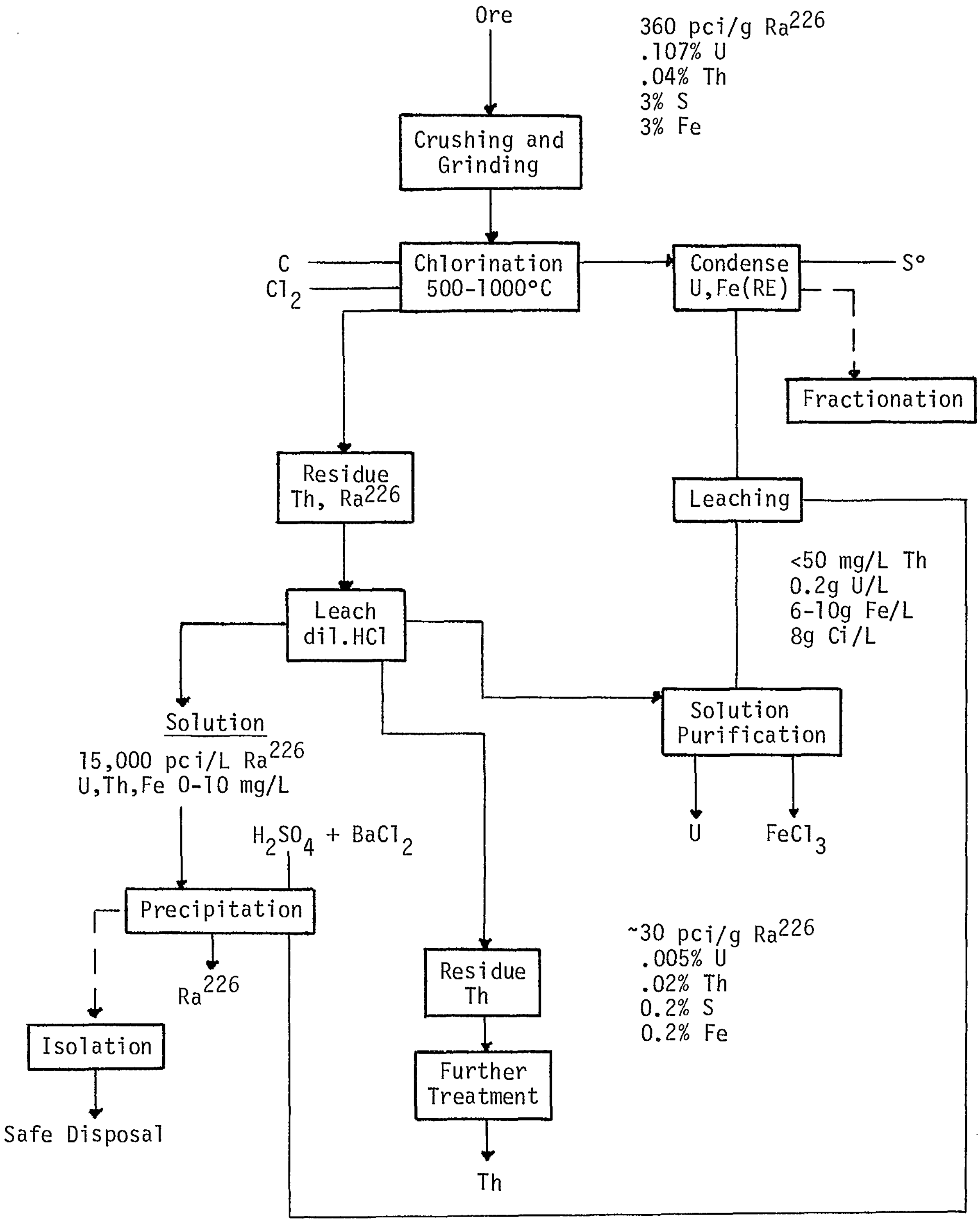


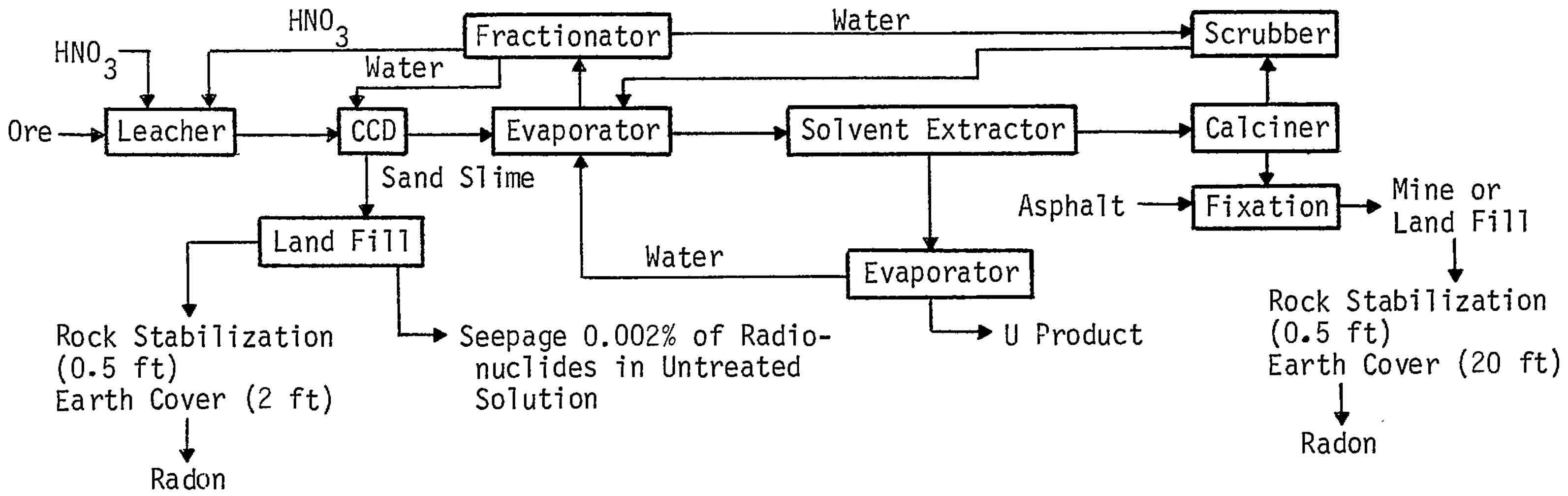
FIGURE 13

SCHEMATIC OF CHLORINATION ROUTE

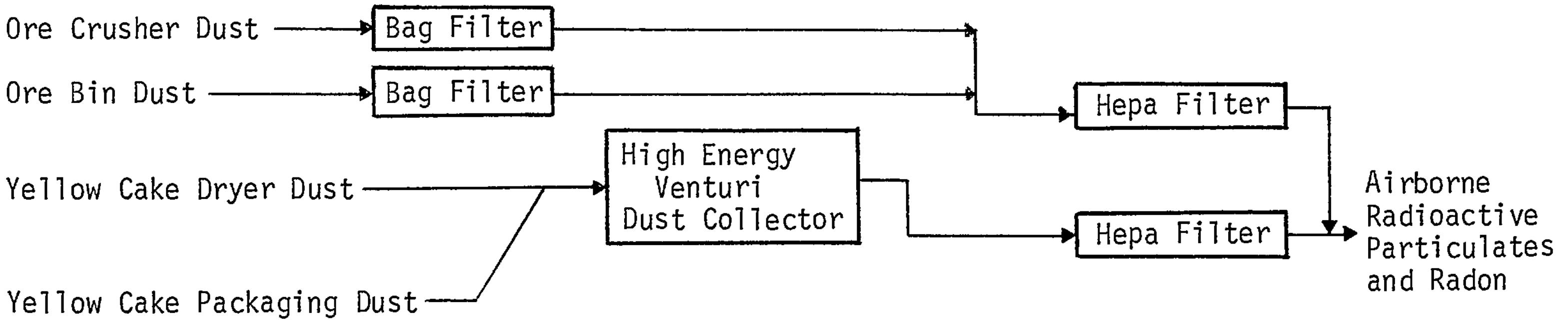
Levins et. al. (45) carried out fundamental studies to determine the factors affecting the leachability of radium 226 from tailings. The major factors identified were pH, solid-liquid ratio, cation and sulfate concentration in solution. A process was proposed for extracting radium from tailings by four stage leaching in 5M NaCl.

11.2 NITRIC ACID PROCESSES

Sears et. al. (38) in a paper study determined the cost and effectiveness of reducing the release of radioactive and non-radioactive materials from model uranium processing mills. One of the processes considered was nitric acid leaching of the ore to remove uranium, radium and other radionuclides in one step. The flowsheet given in Figure (14) proposes leaching ground ore with 3 M nitric acid at $85^{\circ}C$ in a series of agitated tanks. The leached residue is washed in a 10 stage CCD circuit to reduce losses of soluble radionuclides and nitrate to 0.027% of that present in the leach solution. The washed tails are covered with two feet of earth topped by vegetation or coarse rock. The leach liquor is concentrated by evaporation and uranium is recovered by solvent extraction with TBP in kerosene. The vapour from the evaporator is fractionated into water, and 13 M HNO_3, which are recycled to the wash and leach circuits. Uranium is stripped as a concentrated aqueous nitrate solution. The waste raffinate is treated in a continuous calciner to convert the metal nitrates largely calcium, iron, aluminum, and radioactive elements, to oxides and to recover the oxides of nitrogen for recycle as nitric acid. Calcined solids are fixed in asphalt before burial by the method previously described. Most of the equipment is constructed of stainless steel to handle nitric acid.



Liquid and Solid Radwaste Treatment



Airborne Mill Radwaste Treatment

FIGURE 14

NITRIC ACID FLOWSHEET

Capital and operating costs (mid-1973 dollars) for a 2000 ton per day, 4 lbs per ton U_3O_8 model mill operating on the above flowsheet were reported as $24,703,000.00 and $2,226,000.00 calculated capital and operating costs compared to $4,617,000.00 and $1,466,700.00 for sulfuric acid processing (64).

The flowsheet discussed above was based on limited testwork first reported by Seeley (37). Additional leaching studies were carried out and reported by Ryon et. al. (35). No experimental data are presented on the treatment of the leach liquor either for uranium or radionuclide recovery.

Seeley, reported that three stage co-current leaching of Ambrosia Lake sandstone ore at 25 per cent solids for 1 hour at 85°C with 3 M nitric acid removes 93.5 per cent of the radium in the first stage and an additional 1.7 per cent in the other two stages. Similar results were reported for leaching of +150 mesh sand tailings from a sulfuric acid leach process. For acid leach slime tailings (-150 mesh) a single stage nitric acid leach removed only 72 per cent of the radium and 25 per cent was removed in the second stage. These results tend to indicate that in sulfuric acid processing of uranium ore the radium in the slime fraction is present as re-precipitated radium sulfate.

Ryon et. al., reported on nitric acid leaching of uranium ore and mill tailings from five operating mills and tailings from an abandoned mill. Three of the operating mills use sulfuric acid leaching and two use sodium carbonate leaching.

Two stage co-current leaching of ore at 33 per cent solids with 3 M nitric acid for 5 hours at 70°C extracted between 99.5 to 99.7 per cent of the uranium, 85 to 98 per cent of the radium 226, 96 to 98 per cent of the thorium 230. 49 to 86 per cent of the polonium 210 and 25 to 73 per cent of the lead 210. Leached ore residues, in all but one case, exceeded the standard proposed by the United Kingdom for radium 226 in building materials. The radionuclide levels in the residues ranged from 17 to 62 p Ci per g for radium 226; 8 to 32 p Ci per g for thorium 23o; 16 to 140 p Ci per g for polonium 210 and 55 to 120 p Ci per g for lead 210. There was no significant difference in the results for leaching of these radionuclides from the alkaline or acid tailings compared to leaching of the ores.

Attempts to improve the extraction of radium from tailings by roasting with sodium chloride, potassium fluoride or sodium carbonate prior to nitric acid leaching were unsuccessful. Of importance with regards to the potential hazard of handling nitric acid leach residues is the observation that the residual radium is not uniformly distributed throughout the residue. Relatively "hot" sand grains containing more than 50 x 10^6 p Ci of radium per g were isolated from the +100 mesh nitric acid leach residue.

Nitric acid leaching was also studied by Ritcey (10). Laboratory testwork on Elliot Lake, Ontario ore showed that whereas 98 per cent of the uranium and 80 per cent of the thorium were extracted, only 4.9 per cent of the radium 226 was dissolved by leaching with nitric acid. Presumably the poor radium extraction was a result of high sulfate in the leach liquors produced by leaching the pyrite in the ore. Repulping of the leach residues with EDTA solutions was reported to increase the radium extraction to 80 per cent overall. Residues in these experiments at best contained 55 p Ci radium per g. A hydpothetical flowsheet was presented and is reproduced in Figure 15. Isolation of radium and thorium from the leach liquor was not evaluated. A cost estimate (37B) of the process (37C) indicated more than double the capital investment compared to the standard sulphuric acid leach process.

From the published data the following general conclusions are drawn.

- Alternate uranium milling technology, to reduce the short and long term hazards associated with incomplete removal of radionuclides from tailings, is in the early stage of development, but indicates increased recovery of uranium, thorium, increased radium solubility and no sulphates to tailings, compared to conventional.

- The processes suggested by the early reported testwork are complex relative to existing technology.

- The corrosive nature of proposed leachants dictate a substantially higher capital cost relative to existing processes.

- The economic viability of the alternative processes with respect to operating cost, depend on almost total leachant recycle.

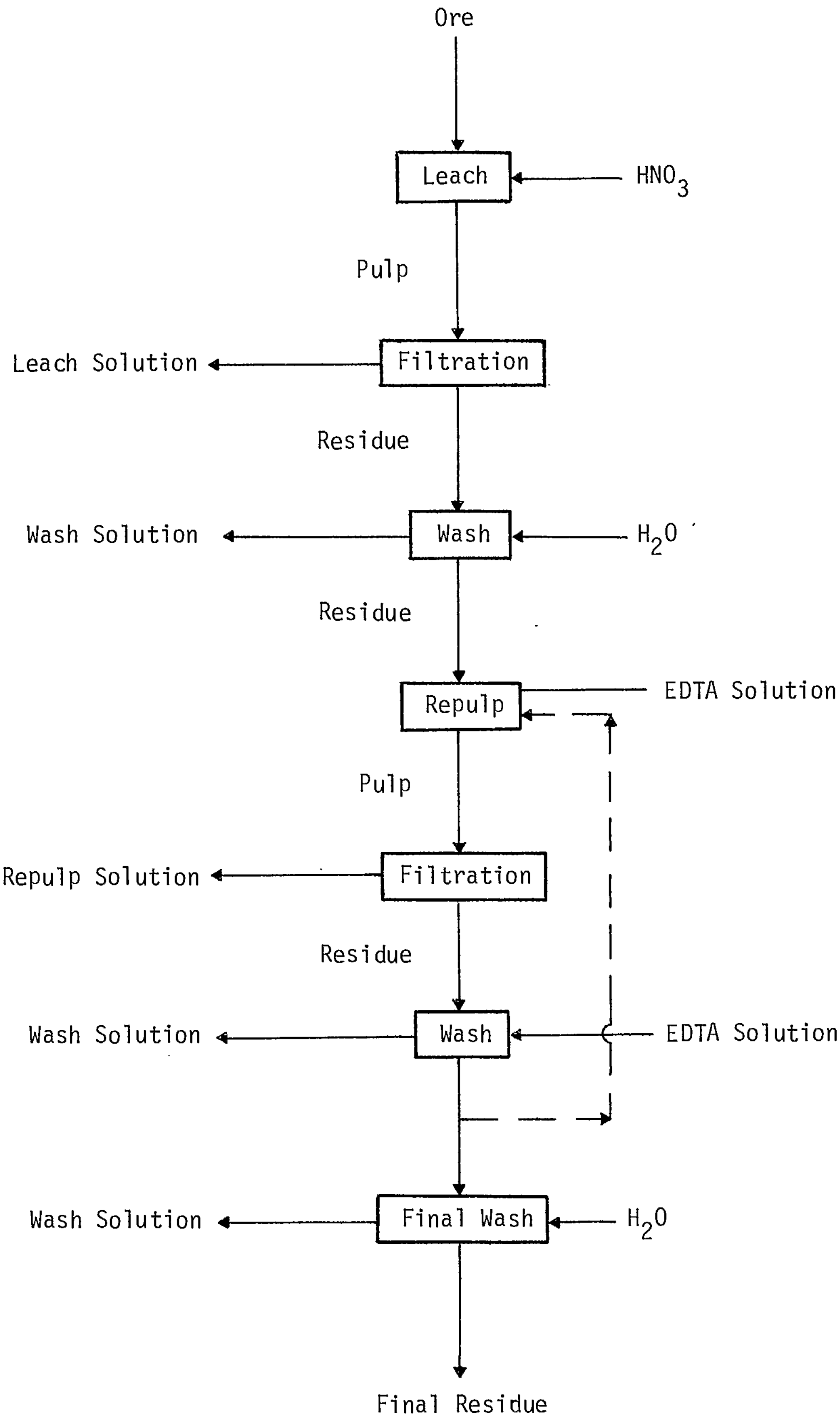


FIGURE 15

CANMET NITRIC ACID LEACH PROCESS

From a technical standpoint it is concluded that:

- A small but significant fraction of radium 226 in uranium ores is highly refractory and its dissolution is not achieved by the suggested processes. A lower level of about 50 p Ci per g radium 226 in final tailings appears practically attainable.

- Proven technology for the isolation of the radionuclides, especially radium 226, from the proposed leachants does not exist. The often mentioned use of sulfate and barium chloride to precipitate barium radium sulfate in isolation from the overall flowsheet is practical, but the build up of sulfate in recycled leachant will reduce leaching efficiency possibly to the point of making the entire process not technically feasible.

- Data must be generated, and the dissolution of thorium 230 and lead 210 by the proposed processes must be ensured, for the long term resolution of the environmental problems associated with radionuclides in uranium extraction.

SECTION III - POTENTIAL OPTIONS FOR RADIONUCLIDE CONTROL

As reported in the previous sections, accepted practice for radionuclide control in conventional mill processes is to: 1) precipitate thorium 230 through neutralization of acid process effluents; 2) radium is removed as barium radium sulfate by the addition of barium chloride to neutralized acid process effluents as well as carbonate process effluents to which sulfate has been added; 3) no specific control procedure has been suggested or employed for lead 210.

Very little information has been published on the recovery of dissolved radionuclides in aqueous liquors produced in the non-conventional milling of uranium ores because of the early stage in the process development at the time of this writing.

For chloride and EDTA based processes, researchers considered sulfate and barium chloride addition to precipitate radium 226. The demonstrated inhibition to radium dissolution by sulfate suggests that this recovery process is of questioned utility. One reference (45) mentions ion exchange as a means of recovering radium 226. No information regarding resin type, loading capacity, etc. is given. Thorium 230 and lead 210 recovery was not considered in those studied surveyed.

Where nitric acid processing of ore was investigated no experimental data were published on the recovery of the dissolved radionuclides. The hypothetical use of calcination to convert the metal nitrates to oxides and recover nitrogen oxide was considered but not tested.

To provide alternatives for the recovery of the dissolved radionuclides from conventional mill tailings effluent and from chloride and nitrate containing leach liquors a review of the chemistry and of analytical procedures for, radium, thorium and lead was carried out.

Separation or isolation methods were analyzed and are reported. Processes used to control the radium content in municipal water supplies were also reviewed and are presented. Processes used to recover thorium from uranium mill residues as well as uranium refinery effluent control procedures were analyzed and pertinent information obtained is reported.

III.I CHEMISTRY

The chemistry of radium, thorium and lead were reviewed so as to provide a basis of evaluating currently accepted practice and alternatives for their removal from chloride, sulfate, nitrate and carbonate liquors produced in current and potential future milling of uranium ores. A brief synopsis of the basic chemistry of the nuclides of interest is given below.

Radium

Radium, atomic number 88, is the heaviest of the alkaline earth group. Included in this group are the elements beryllium, magnesium, calcium, strontium and barium.

All isotopes of radium are radioactive, having half-lives of between 3.64 days (radium 224) to 1622 years (radium 226).

The chemistry of radium follows closely that of barium.

The only known oxidation state of radium is +2 and its standard reduction potential, calculated from thermodyanamic data, is -2.92 V (65). The potential for barium is slightly more positive, -2.90 V.

Radium forms an amalgam, and was first prepared by electrolysis of the chloride at a mercury electrode. Pure radium was obtained by vacuum distillation of the mercury. (65).

The radius of the radium^{+2} ion has been calculated to be 1.52 Å (116). X-ray crystallographic studies of radium fluoride give a value of 1.37 Å(65). The ionic radius of barium is 1.35 Å (65). The crystal radius of radium metal has been calculated to be 2.35 Å compared to 2.17 Å for barium. The radii of the hydrated alkaline earth ions are in the order Ca>Sr>Ba>Ra.

The ionic radius of radium being somewhat larger than that of barium or calcium (1.06 Å), and radium being the least hydrated of the alkaline earth metal ions and therefore more mobile, thus radium should be more strongly adsorbed on ion exchange resins.

Radium shows no tendency to form anionic complexes with either nitrate or chlorides. With EDTA, anionic complex formation is reported. (65).

The solubilities of radium compounds are usually inferred from the solubility of the corresponding barium salt and the trend in solubilities of the alkaline earth compounds. Thus the solubility of radium hydroxide is greater than any of the other alkaline earth hydroxides and the sulfate is the least soluble.

The solubility product for radium sulfate has been reported at 4.25×10^{-11} at 20°C (20). This corresponds with a solubility of 2.1×10^{-3}g per 1 water.

Radium chloride and nitrate are insoluble in highly concentrated hydrochloric and nitric acids but are soluble in water. Erbacher (117) reported that the water solubility at 20°C of radium chloride and nitrate are 24.5 and 13.9 g per 100 g water respectively.

Other slightly water soluble radium salts include the fluoride, phosphate, oxalate, carbonate, iodate, chromate, selenate, tellurate and fluoroberyllate (65).

Like the other alkaline earth metals, radium forms few complexes in acid solution. In alkaline solution complexes are formed with many organic ligands. Sedlet (65) has compared the formation constants of some radium complexes with those for the other alkaline earths. For a given ligand the formation constant generally decreases in the order calcium>magnesium>strontonium>barium >radium i.e. radium forms the weakest complex.

Thorium

Thorium, atomic number 90, is a member of the actinide family of metals which includes uranium.

Naturally occurring isotopes of thorium, in the decay series of uranium, thorium or actinium series, include thorium 234, thorium 232, thorium 231, thorium 230 (ionium), thorium 228 and thorium 227. Half-lives for these isotopes vary from a low of 25.64 hr (thorium 231) to a high of 80,000 years (thorium 230).

In aqueous solution the stable oxidation state of thorium is +4. Its standard reduction potential is -2.06 V (68).

The ionic radius of thorium (IV) is given as 1.10 Å whereas the crystal radius of the metal is 1.82 Å (68). The smaller ionic radius of thorium, compared to radium, would suggest that the radius of hydrated thorium is greater than radium.

Thorium, because of its charge, is expected to be strongly adsorbed on cation exchange resins. The larger degree of hydration of thorium relative to radium would reduce its mobility and somewhat offset the strong adsorption expected because of the higher charge on thorium.

Thorium forms a large number of inorganic complexes in aqueous solution, few of which are anionic (68).

With chloride, thorium shows little tendency to form anionic complexes. Formation constants for the mono-, di-, tri-tetra- and penta-chloro species are reported as, 1.58, 10×10^{-1}, 8.9×10^{-1}, 2.5×10^{-1} and 9.9×10^{-2} respectively (118).

Anionic complexes of thorium with nitrate have been inferred from its strong adsorption onto anion exchange resins from 6 to 8N nitric acid solutions (68).

Thorium also forms many complexes with organic ligands. Numerous solvent extraction procedures for use in analytical chemistry, based on chelate formation have been reported (78).

Insoluble salts of thorium form readily with hydroxide, fluoride, oxalate and other common precipitants.

Precipitation of thorium as a hydrous hydrate begins at pH3 and is reported to be complete at pH6 (68). Excess alkali is required to precipitate thorium from high sulfate solutions, presumably due to the presence of thorium sulfate complexes. The solubility product for thorium hydroxide ($ThO(OH)_2$) is reported as 5.5×10^{-24} (119).

Thorium sulfate may crystallize with two, four, six, eight or nine molecules of water. Reported solubility of the octahydrate at 30°C is 2 per cent thorium sulfate in 0 to 10 per cent sulfuric acid decreasing to 0.08 per cent in 38 per cent sulfuric acid (68).

Thorium nitrate is very soluble in water (65.6 g per 100 g solution at 20°C). (68). This high solubility permits its extraction using TBP as a solvent.

Lead

Lead, atomic number 82, has five radioactive isotopes with half-lives ranging from 36.1 minutes lead (211) to 19.4 years lead (210).

Lead, in solution, exists in two well defined oxidation states, lead (+2) and lead (+4). Lead (+2) is the more common of the two oxidation states. The standard reduction potential for lead (+2) to metal is -0.126 V and lead (+2) to lead (+2) is ca. 1.7 V (74).

The ionic radius for lead (+2) is reported to be 1.18Å and for lead (+4) 0.70Å (120) indicating that the degree of hydration for lead (+2) is less than thorium (+4) but greater than radium (+2).

Lead (+4) compounds are produced by oxidation of lead (+2) with solution chlorate, permanganate or peroxide to produce lead dioxide. Compounds with lead in the +4 state are very strong oxidants giving lead (+2) on reduction. In concentrated hydrochloric acid, anionic complexes are believed to be formed. The hydroxide is amphoteric and dissolves in dilute caustic to give $Pb\ (OH)_6^{2-}$ or PbO_3^{2-} (74).

Lead (+2) precipitates from solution as a slightly soluble hydroxide, carbonate, sulfate, chloride and nitrate.

Lead (+2) hydroxide has a reported solubility product of 4.0 x10^{-15} (120). The precipitated hydroxide is amphotheric dissolving in dilute solutions of base to give $HPbO_2^-$ or PbO_2^{2-} ions. Lead (+2) carbonate has a solubility product of 1 x 10^{-13} (120).

The solubility product for lead (+2) sulfate is reported as 1.6 x 10^{-8} (120). Its solubility has been reported to increase with increasing sulfuric acid to a maximum of 6.68 ppm in 10 per cent acid. (75).

Lead (+2) chloride is slightly soluble in water having a solubility product of 2.6 x 10^{-5}. In excess chloride, dissolution of the precipitate occurs due to complex ion formation. Anionic lead chloro complexes are well reported in the literature. The formation constants for the mono-, di-, tri-, and tetra-chloro species are 14.5, 3.5, 1.8 and 5.5 x 10^{-2} respectively (118). Lead chloro complexes adsorb readily on anion exchange resins and are extracted with quarternary amine chlorides.

Lead (+2) nitrate is readily soluble in water having a reported solubility of 5.6 x 10^{-2} (120). It is insoluble in concentrated nitric acid and is reported to quantitatively precipitate from this medium (74). Formation constants reported (120) for the mono-, di-, tri- and tetra- nitrate complexes are 3.2, 3.2 x 10^{-1}, 1.3 respectively, indicating that only weak anionic complexes with nitrate are formed.

111.2 RADIONUCLIDE RECOVERY

Radium, thorium and lead are recovered from aqueous solutions by one of precipitation, solvent extraction or ion exchange.

Precipitation

1. Radium

Since radium occurs only in trace concentrations, co-precipitation with a carrier is usually the initial step in a separation-purification scheme. Most metal ion sulfates are soluble. Therefore, co-precipitation with lead or barium sulfate has been very useful for separating radium from macroscopic amounts of most other metal ions. Lead is used if a carrier-free radium fraction is desired since quantitative separation of lead and radium are possible while the separation of barium from radium is difficult.

Precipitation of radium is carried out from slightly acid solutions by adding an excess of sulfuric acid or soluble sulfate to a solution containing lead or barium ions. Significant quantities of thorium 230 (0.5%) are reported to precipitate as well (20).

Co-precipitation with barium chloride has been used to determine radium in sulfate free solutions (65). Precipitation was carried out by adding an excess of concentrated hydrochloric acid-ethyl ether solution to an acid solution of the sample containing barium carrier. Barium radium chloride is precipitated.

Co-precipitation of barium or lead radium nitrate has been reported (20, 65). Since radium nitrate is soluble, nitric acid concentrations of at least 70 per cent are used.

A summary of the co-precipitation behaviour of radium was given by Sedlet (65). A general discussion of co-precipitation has been given by Hahn (66) and Bonner and Kohn (67). Co-precipitation of radium with barium as it relates to isomorphous replacement or adsorption of radium on barium sulfate has been discussed in WIN 112 (20).

2. Thorium

Precipitation with oxalate, fluoride, ammonia, peroxide, iodate and organic acids have been used in thorium analyses (68).

Oxalate precipitates thorium from acid solutions. Uranium (IV) and the rare earths are co-precipitated. High concentrations of calcium, lead, copper and strontium in solution will result in their precipitation as well.

Oxalate precipitation has been suggested for thorium recovery from uranothorianite ores and wastes from radium processing plants.

Brodsky (69) proposed dissolving uranothorianite ores in 1:1 nitric acid, co-extracting uranium and thorium with TBP after acid neutralization to give a final acidity of 1.5 and 1.8 N, stripping the loaded solvent with acidified water and precipitating thorium with oxalic acid dihydrate at 90°C. Oxalic acid consumptions were reported as 1 kg per kg thorium oxide in solution. About 99 per cent of the thorium in solution was recovered.

Van Cleave (70), carrying out laboratory studies on thorium 230 recovery from pitchblende residues, reported its precipitation from 2N nitric acid by adding oxalic acid.

Carswell (71), studying the recovery of thorium 230 from uranium wastes, reports that thorium nitrate in TBP is precipitated by contact with oxalic acid solution.

Precipitation of thorium with hydrofluoric acid gives about the same separation as with oxalic acid. Hydrofluoric acid is the preferred reagent for concentration in trace analysis.

Peppard (72) described a process whereby thorium 230 is extracted from 0.1 nitric acid using TBP. The loaded organic is stripped with hydrofluoric acid to precipitate thorium fluoride which is recovered in a continuous centrifuge.

Brodsky (69) reported on the recovery of thorium as a fluoride by precipitation at pH 2.

Perkins (73) precipitated trace thorium from 2N nitric acid with hydrochloric acid.

Thorium is quantitatively precipitated with base e.g. ammonia caustic, or lime. This is the method used to control thorium in acid mill effluents.

In the absence of phosphate and sulfate, thorium is quantitatively precipitated with hexamethylene - tetramine (68).

Hydrogen peroxide has been used to precipitate thorium as the peroxynitrate from 0.03 N nitric acid (68).

Iodate also has been used to precipitate thorium from nitric acid solutions (68).

Finally a large number of organic acids have been proposed for the precipitation of thorium and its separation from rare earths (68).

3. Lead

Analysis of lead by precipitation as a sulfate, chromate or molybdate has been reviewed (74).

Craig (75) measured the solubility of lead in sulfuric acid solutions of varying concentrations. Lead solubility was found to decrease with increasing sulphuric acid reaching a minimum at 0.3 per cent sulfuric acid (4.55 ppm lead in solution) after which the solubility increases to reach a maximum at 10 per cent sulfuric acid (6.68 ppm) and then decreases again.

Lead chromate is less soluble than the sulfate as is lead molybdate which is the most insoluble of the three.

Willard reported that lead is quantitatively precipitated from 84 per cent nitric acid as the nitrate.

Kallmann (77) reported on the precipitation of lead chloride from a 2 per cent solution of hydrochloric acid in n-butanol.

Solvent Extraction

1. Radium

Analytical procedures for radium, utilizating solvent extraction have, in all cases, involved the extraction of interfering ions, leaving radium in aqueous solution. It has been reported (65) that organic phosphates, thenoyltrifluoroacetone (TTA) and high molecular weight amines do not extract radium.

2. Thorium

Thorium recovery, by solvent extraction from the nitric acid process streams, shows promise. Extensive use of solvent extraction has been made both in analysis and processing of thorium-containing wastes.

De et. al. (78) in their book on "Solvent Extractions of Metals" reviewed extractants and their use in analytical chemistry. References to analytical procedures include the use of β-diketones, hydroxyquinolines, hydroxlamines, nitrosophenols, organophosphorus compounds, amines and phenylarsonium compounds to extract thorium from aqueous solution.

Tributyl phosphate (TBP) extraction of thorium from nitric acid solutions has been studied extensively.

Grimaldi (68) reviewed the influence of TBP, nitric acid, total nitrate and thorium concentration on the extractability of thorium. Extraction is improved by increasing any or all of the above.

The utility of solvent extraction for thorium removal from nitric acid process liquors is demonstrated by its use in pilot scale processing of pitchblende residues and other thorium-containing materials.

Brodsky (69), Carswell (71, 79) and Peppared (72) reported on the recovery of thorium from nitric acid solutions by solvent extraction with TBP. Diamylamyl phosphate was used by National Lead Co. to refine thorium dissolved in nitric acid (80). No information is given in these references on residual thorium in raffinates.

For hydrochloric acid process liquors, Grimaldi (68) reports that thorium extraction by TBP becomes appreciable only at acid concentrations exceeding 8 N. Distribution ratios of thorium into undiluted TBP were reported to vary from less than 0.001 at 2 N HCl to about 0.5 at 8 N and increasing to more than 20 at 12 N HCl.

At Elliot Lake, Ontario, thorium was recovered from acid sulfate uranium leach solutions after ion exchange removal of uranium by solvent extraction with an organic phosphorus reagent. Loaded thorium was stripped with 10 N sulfuric acid to simultaneously precipitate thorium from the organic phase (112).

3. Lead

Analytical procedures for lead, utilizing solvent extraction, are numerous. Extraction from neutral and basic solutions using β-diketones, hydroxyquinoline cupferron, nitrosophenols, dithizone and dithiocabamates have been reported (78). Aliquat 336, Amberlite LA-1 and D_2EHPA have been used to extract lead from 1.8 M, 1.5 M and 0.1 M hydrochloric acid solutions respectively. (78, 113).

Ion Exchange

The use of ion exchange to recover radium 226, thorium 230 and lead 210 from conventional and non-conventional uranium process liquors appears promising. Cation exchange is used in municipal water treatment plants to remove radium from well waters (81). Anion exchange has been used in analysis, as a means of separating the radionuclides dissolved in nitrate and chloride media (82).

The difference in ion exchange behaviour of the three nuclides is related to their chemistry.

Radium forms few strong anionic complexes in acid solution and is therefore not adsorbed on anion exchange resins unless it is in the form of EDTA or citrate complexes (65). Thorium on the other hand forms anionic complexes with nitrate but not chloride complexes in solutions up to 6 M hydrochloric acid (83). Lead behaves opposite to thorium i.e., it forms strong anionic chloride complexes but not nitrate complexes (83).

Athvale et. al. (82) used the differences in the radionuclides complexation chemistry to analyze uranium and its daughter products by ion exchange on Amberlite IRA 400 anion exchange resin. Lead 210 was adsorbed from 1.5 M hydrochloric acid and thorium 230 from 8 M nitric acid. Radium 226 was not adsorbed.

Other ion exchange studies are reviewed below:

Sulfate Media

1. Radium

The recovery of radium by adsorption on zeolites (86), natural and synthetic permutites (84, 86), and alumina (85) has been known for some time.

Laboratory tests conducted by Arnold and Crouse (87) showed the potential utility of removing radium 226 from lime neutralized acid leach effluents by adsorption on synthetic and natural zeolites.

Batch adsorption tests on a solution containing 4100 p Ci per l radium 226 showed that clinoptilolite (natural zeolite), Decalso (synthetic zeolite), Linde Molecular Sieves A W - 500 and 13 x 9A, barite, zirconium phosphate and tungstate, barium phytate and a phosphoric acid ion exchange resin had high radium loading capacities. Radium loading was in the range 2000 to 3100 p Ci per g exchanger. It was inferred that thorium 230 was not extracted.

Further testing of barite, Decalso and clinoptilolite under continuous column operation was carried out on a feed containing 2300 p Ci per l radium 226. At column throughputs of 1.5 USGPM per ft^2, breakthrough of radium (effluent 10 p Ci per l) occurred after 3000 bed volumes for barite, 2600 bed volumes for Decalso and 480 bed volumes for clinoptilolite. Calculated radium loading at radium breakthrough were 6×10^6 p Ci per l wet-settled barite and Decalso and 1.1×10^6 p Ci per l wet-settled clinoptilolite.

Ammonium nitrate was shown to effectively strip radium from clinoptilolite but not from the other two exchangers. Radium in the strip liquor (900,000 p Ci per l) was precipitated by adding 0.02 M ammonium sulfate and stoichiometric barium nitrate to give a granular, rapid settling barium radium sulfate.

Other references to removal of radium from sulfate media by ion exchange include the analysis of total radium by methathesis of barium radium sulfate onto a cation exchange resin (27). Also the use of ion exchange to treat runoff and seepage to be produced by Ranger Uranium Mines Pty. Ltd. was inferred by A. H. Ross and Associates (88). No experimental data were given. Finally in WIN 117 (89) it was reported that radium 226, in acid mill effluents, adsorb on glass wool and polyethylene shavings to the extent that 55 per cent of the activity was removed. About 50 per cent of the adsorbed radium could be removed by washing with 2 M nitric acid.

2. Thorium

Thorium and other tetravalent ions have a strong affinity for strong acid cation exchange resins. Kuralova (90, 91) showed that thorium 230 (in sulfuric acid solutions at or below 0.1 N) is quantitatively adsorbed onto KU-2 cation exchange resins. Increasing the sulfuric acid concentration adversely affected the adsorption. Stripping of loaded thorium could be accomplished with saturated ammonium carbonate but not with nitric acid.

Stripping of thorium adsorbed on cation exchange resins has also been reported using sodium bisulfate, 3 M sulfuric acid, 6 M sulfuric acid and citrate buffers (68).

Thorium in sulfate media has also been reported to adsorb on anion exchange resins.

Tame and Rosenbaum (92) reported that for resin-in-pulp processing of uranium mill acid leach liquor, 18 to 25% of the thorium 230 is adsorbed on IRA 425 anion exchange resin.

Karalova (90) reported that for solutions containing 12 N sulfuric acid, 20 per cent of the thorium is adsorbed on AV-17 anion exchange resin. Below 4 N sulfuric acid, no thorium is removed from solution.

3. Lead

Few references were obtained on the use of ion exchange to recover lead from sulfate media due presumably to its low solubility.

The separation of lead from various elements by adsorption on strong acid cation exchangers was studied by Khopkar and De (93). Lead is easily eluted with ammonium acetate making the separation of lead from strontium, barium and aluminium feasible.

Nitrate Media

Ichikawa et. al. (94) surveyed the distribution of metal ions between the anion resin Dowex 1 and solutions varying in nitric acid content. Their data is reproduced in Figure 16. It is important to note that whereas thorium is strongly adsorbed, the distribution co-efficients for lead and radium fall well below calcium. Thus if nitric acid leach liquors were high in calcium, anion exchange would not be effective in removing lead and radium.

Other ion exchange data obtained from the literature are given below:

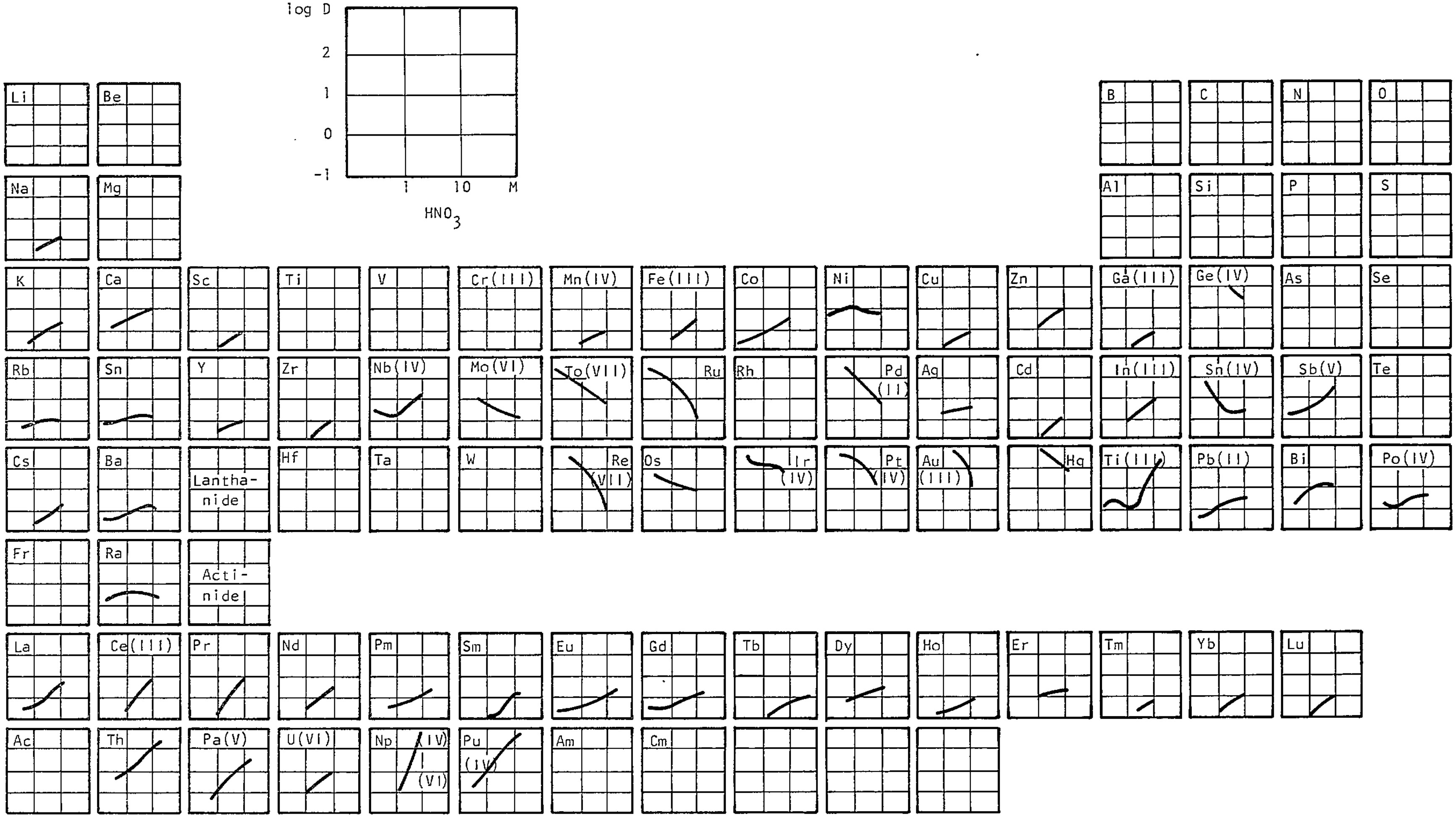


FIGURE 16

WEIGHT DISTRIBUTION COEFFICIENTS (D) IN NITRIC ACID [DOWEX 1 X - 8]

1. Radium

Limited data in the literature indicate that radium can be removed from dilute nitric acid solutions by adsorption onto strong acid resins.

Tompkins (95) patented the separation of micro amounts of radium from macro amounts of barium in nitrate and chloride media by ion exchange on a sulfuric acid cation exchange resin. Stage-wise elution of barium followed by radium used citrate, oxalate, malonate etc.

Hagemann (96) reported that if a mixture of thorium, radium and actinium in 2 M nitric acid is passed through a column of Dowex 50 (strong acid resin), radium will be partially adsorbed while the others will be completely adsorbed. Continued washing of the resin with 2 M nitric acid removes all the radium. These observations relate to the different affinities of cation exchange resins for di-, tri- and tetravalent ions.

Similarly, Van Cleave (70) reported on the removal of both radium 223 and thorium 230 from nitric acid leach liquors produced in the extraction of thorium from pitchblende residues. Radium was eluted from the column with 4 N nitric acid whereas sodium bisulfate was required to elute the adsorbed thorium.

2. Thorium

Thorium in nitric acid is strongly adsorbed on both cation and anion exchange resins.

Reference has already been made to adsorption on cation exchange resins as studied by Hagemann (96) and Van Cleave (70).

Bush (97), on the analysis of thorium 230 in uranium ores, reports that thorium is loaded onto AG1 anion resin and elution is accomplished with 1.5 N hydrochloric acid. Similarly, adsorption of thorium 230 from 0.1 N nitric acid onto an anion exchange resin was used for analysis as reported in WIN 121 (51).

Carswell (98) has indicated the feasibility of separating thorium from uranium (IV) by adsorption of both from 6 to 8 M nitric acid on De-acidite FF anion exchange resin. Uranium is first eluted with 4 M nitric acid and thorium is then stripped from the resin using water.

Finally, the work of Dai (99) indicates that thorium in nitric acid can be adsorbed on weak acid ion exchangers.

3. Lead

The only reference to the ion exchange behaviour of lead in nitrate media, besides the previously mentioned Athvale et. al.

paper (82), shows that lead in 6 M nitric acid is not adsorbed on anion exchange resins (100).

Presumably lead could be recovered from nitric acid by adsorption on cation exchange resins.

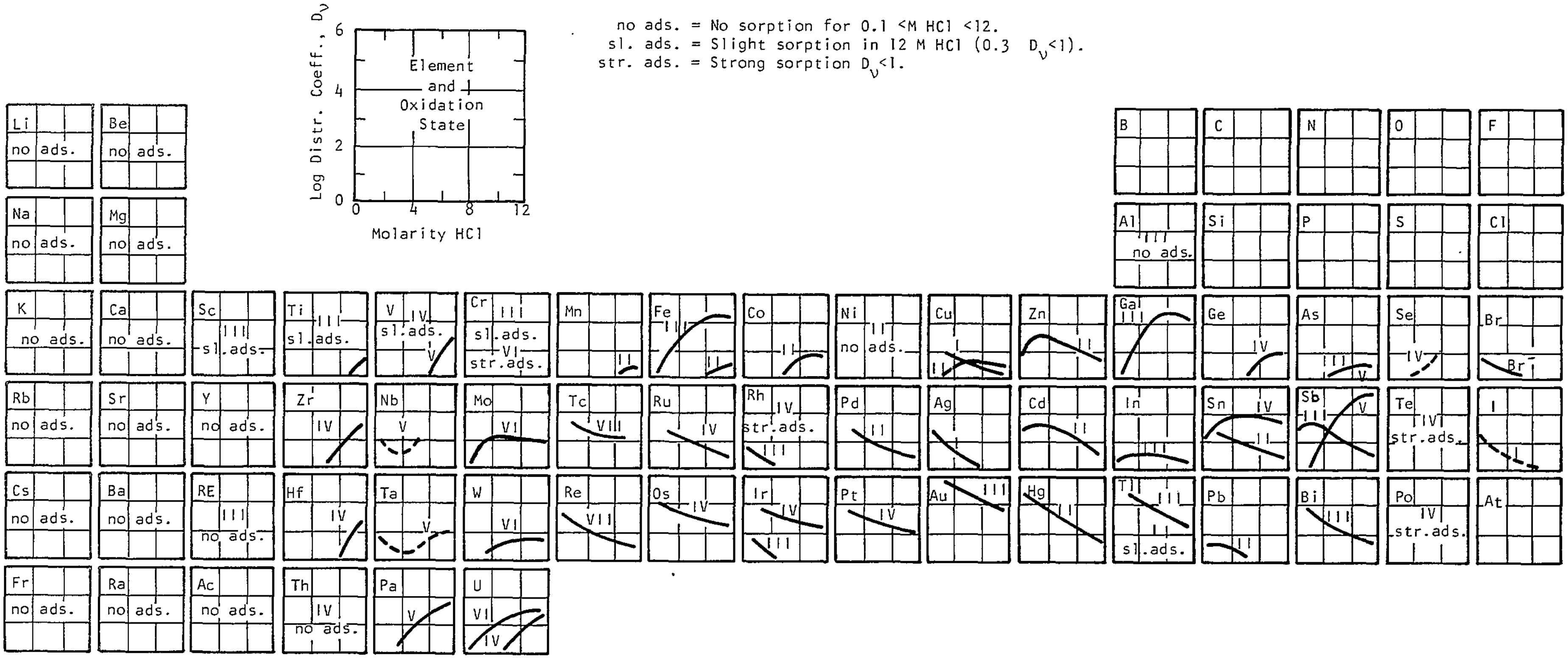
Chloride Media

The anion exchange behaviour of metal ions in hydrochloric acid has been reviewed by Kraus and Nelson (101). Their survey, reproduced in Figure 17, shows that whereas radium and thorium do not adsorb on Dowex 1, lead can be extracted from hydrochloric acid media.

Other data on the ion exchange behaviour of the nuclides of interest are given below:

1. Radium

Diamond (102) studied hydrochloric acid elution of alkaline earth and alkali ions adsorbed on Dowex 50 cation resin. Plots of fraction of metal per gram resin divided by fraction of metal per ml eluant, (distribution ratio) versus molarity of hydrochloric acid in eluant indicate that radium could be separated from calcium in solutions containing less than 8.7 M hydrochloric acid. Up to this acid concentration the order of retention on the resin was radium >>calcium >sodium. Above 8.7 M hydrochloric acid calcium is more strongly held on the resin than is radium. This



no ads. = No sorption for 0.1 <M HCl <12.
sl. ads. = Slight sorption in 12 M HCl (0.3 D_v<1).
str. ads. = Strong sorption D_v<1.

FIGURE 17

VOLUME DISTRIBUTION COEFFICIENTS (D_v) IN HYDROCHLORIC ACID [DOWEX X - 10].

reversal at high acid levels is probably due to partial dehydration of the ions.

O'Janne (103) studied the distribution of the alkaline earths between Dowex A-1, chelating resin based on nitrilodiacetate, and glycine-hydrochloric acid mixtures. At constant acid concentration, adsorption by the resin was in the order radium >calcium>magnesium.

Germain (104) reported on the adsorption of radium from chloride solutions onto barium sulfate. The capacity of the solid was reported to be 50,000 p Ci radium per gm adsorbent.

Levins (45) stated that radium 226 could be recovered from strong brine solutions, by ion exchange but no data regarding resin type, etc. were presented.

2. Thorium

Thorium has little tendency to form anionic complexes with chloride. Kraus et. al. (105) showed that for hydrochloric acid solutions, in the range 0.1 to 12 M, adsorption of thorium on the strong base anion exchanger Dowex 1 is negligible.

Thorium should adsorb on cation exchange resins. Grimaldi (68) reports that thorium adsorbed on sulfonic acid ion exchange resins cannot be eluted with 2 to 3 N hydrochloric acid.

3. Lead

Much of what has been reported on the ion exchange behaviour of lead is involved with its extraction from chloride media.

Carrier-free radium solutions have been produced by adsorption of anionic lead chloro complexes on anion exchange resins (20, 106). Radium is not adsorbed.

Kraus and Nelson (101) showed that adsorption of lead from hydrochloric acid media onto Dowex 1 anion exchange resin reaches a maximum at about 2 M acid. Above 2 M hydrochloric acid, lead extraction decreases„ such that at 8 M acid, lead is not adsorbed. Yoshina and Kojima (107) took advantage of this in their method for determining tin and antimony in metallic lead. The sample, dissolved in 12 M hydrochloric acid, when passed through an anion exchange resin loaded tin and antimony leaving lead in solution.

Lead in hydrochloric acid media can also be adsorbed onto Dowex 50 cation exchange resin. Strelow (108) presented equilibrium distribution co-efficients for about 40 elements at different concentrations of hydrochloric acid. The data (Table 14) shows the potential of using cation exchange to remove thorium and lead from chloride media.

TABLE 14

WEIGHT DISTRIBUTION COEFFICIENTS (D) AT DIFFERENT NORMALITIES OF HYDROCHLORIC ACID[DOWEX 50 X - 8].

Cation	0.1	0.2	0.5	1.0	2.0	3.0	4.0
ZrO^{+2}	$>10^5$	$>10^5$	$\sim 10^5$	7250	489	61	14.5
Th^{+4}	$>10^5$	$>10^5$	$\sim 10^5$	2049	239	114	67
La^{+3}	$>10^5$	10^5	2480	265.1	48	18.8	10.4
Ce^{+3}	$>10^5$	10^5	2460	264.8	48	18.8	10.5
Y^{+3}	$>10^5$	$>10^4$	1460	144.6	29.7	13.6	8.6
Ba^{+2}	$>10^4$	2930	590	126.9	36	18.5	11.9
Hg^{+}[a]	$>10^4$	7600	640	94.2	33	19.2	13.6
Al^{+3}	8200	1900	318	60.8	12.5	4.7	2.8
Sr^{+2}	4700	1070	217	60.2	17.8	10.0	7.5
Ga^{+3}	$>10^4$	3036	260	42.58	7.75	3.2	0.36
Ca^{+2}	3200	790	151	42.29	12.2	7.3	5.0
Pb^{+2}[a]	$>10^4$	1420	183	35.66	9.8	6.8	4.5
Fe^{+3}	9000	3400	225	35.45	5.2	3.6	2.0
Cr^{+3}	1130	262	73	26.69[b]	7.9	4.8	2.7
Tl^{+}[a]	173	91	41	22.32	9.9	5.8	3.3
Ni^{+2}	1600	450	70	21.85	7.2	4.7	3.1
Co^{+2}	1650	460	72	21.29	6.7	4.2	3.0
Mg^{+2}	1720	530	88	20.99	6.2	3.5	3.5
Mn^{+2}	2230	610	84	20.17	6.0	3.9	2.5
Fe^{+2}	1820	370	66	19.77	4.1	2.7	1.8
Cs^{+}	182	99	44	19.41	10.4	...	...
UO_2^{+2}	5460	860	102	19.20	7.3	4.9	3.3
Ag^{+}[a]	156	83	35	18.08	7.9	5.4	4.0
Cu^{+2}	1510	420	65	17.50	4.3	2.8	1.8
Hg^{+2}[a]	4700	1090	121	16.85	5.9	3.9	2.8
Zn^{+2}	1850	510	64	16.03	3.7	2.4	1.6
Rb^{+}	120	72	33	15.43	8.1	...	...
K^{+}	106	64	29	13.87	7.4	...	...
Be^{+2}	255	117	42	13.33	5.2	3.3	2.4
Ti^{+4}	$>10^4$	297	39	11.86	3.7	2.4	1.7
V^{+4}		230	44	7.20	...	...	...
Na^{+}	52	28.3	12	5.59	3.6	...	...
Li^{+}	33	18.9	8.1	3.83	2.5	...	...
Sn^{+4}	$\sim 10^4$	45	6.2	1.60	1.2	...	...
Cd^{+2}	510	84	6.5	1.54	1.0	0.6	...
V^{+5}	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Mo^{+6}	10.9	4.5	0.3	0.81	0.2	0.4	0.3
Se^{+4}	1.1	0.6	0.8	0.63	1.0	...	0.7
Bi^{+3}	Ppt.	Ppt.	<1.0	1.0	1.0	1.0	1.0
As^{+3}	1.4	1.6	2.2	3.81	2.2	...	...
Sb^{+3}	Ppt.	Ppt.	Ppt.	Ppt.	2.8	...	...
Pt^{+4}	...	...	...	1.4	...	...	...
Au^{+3}	0.5	0.1	0.4	0.84	1.0	0.7	0.2
Hg^{+2}	1.6	0.9	0.5	0.28	0.3	0.2	0.2

[a] Done in nitric acid.
[b] More than one cationic species present.

Other Media

Kellex Corporation (109) reported that batch contact with Dowex 50 strong acid resin removed 80 per cent of radium in an EDTA leach liquor at pH 6.1. Increasing the pH of the liquor to 8 reduced the radium extraction to zero per cent.

Kozak (110) reported that ion exchange, with Duolite ES-63 phosphoric acid exchanger, reduced lead in effluent streams from an initial 40 ppm to less than 0.05 ppm. Lead in the waste streams was present as a 2 - ethyl hexoate and salicylate.

Ion exchange, using strong acid resins, has been shown to be effective in removing radium 226 in municipal water treatment plants.

The Iowa Department of Environmental Quality, Des Moines determined radium removal efficiencies in nine municipal water treatment plants (81). Four of these plants used strong acid polystyrene ion exchange water softeners in their water treatment plants. Resins used were Dowex HCR, Permutit - Q and a Amberlite resin. All ion exchange softeners were of the pressure type in vertical steel shells. (See Figure 18).

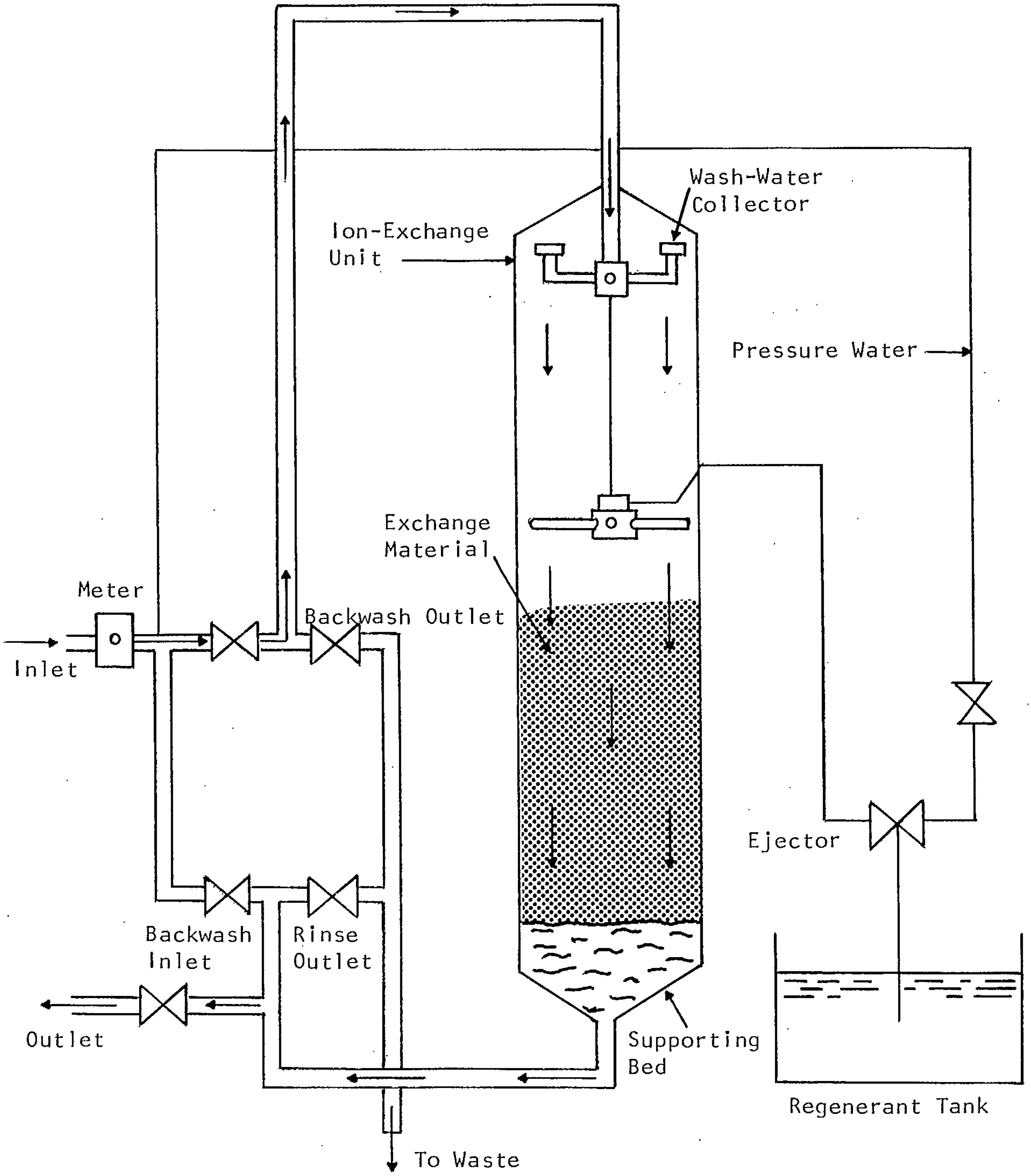


FIGURE 18

DIAGRAM OF TYPICAL ION EXCHANGE UNIT

Removal of radium 226 was excellent. Removal efficiencies between 93 to 95% with effluents analyzing from 0.2 to 1.9 p Ci per l were obtained from feeds analyzing 4.9 to 43 p Ci per l radium 226. Calcium and magnesium were reduced from about 90 and 40 ppm respectively to 3 and 1 ppm respectively.

Data obtained by running the softeners 10% past normal regeneration time indicated continued radium removal after the hardness removal capacity was exhausted.

Brine regeneration of the resins produced liquors containing up to 3150 p Ci per l radium 226. Salt utilization was about 50 per cent.

Core samples of the resin bed after backwash, showed a concentration of radium in the lower reaches of the bed. Ion exchange bed analysis are given below.

Ion Exchange Core	Ra 226 (p Ci per gm dry resin)	Ra 228 (p Ci per gm dry resin)
Top	79.4	26.7
Middle	72.2	23.6
Bottom	116.4	34.7

It was concluded that a substantial residual of radioactivity is retained in the ion exchange resin beads and is not removed during regeneration.

Radium removal, utilizing ion exchange for municipal water treatment, is also practiced in Illinois and Florida. Radium removal efficiencies in these plants and those in Iowa are given in Table 15 (112).

In all cases soluble radium in the final effluent was substantially below the Province of Ontario Guideline of 3 p Ci per l radium 226.

Other Radionuclide Removal Processes

Other unit operations employed in water treatment plants were also found to be effective in removing radium 226 from well water. Data given in the Iowa Department of Environmental Quality survey (8) of radium removal efficiencies in water treatment plants showed the following:

Aeration - retention followed by filtration removed from 12 to 45% of the well water radium, presumably by adsorption or the action of oxidation products deposited on the filter media. Anthracite filter media, after use, analyzed 225 and 72 p Ci per g radium 226 and 228, respectively.

Reverse Osmosis (one plant) was found to reduce the radium content of the well water from 14 p Ci per l to 0.6 p Ci per l giving a radium removal of 96%. Concentrate analyzed from 38 to 56 p Ci per l radium. Permeate relative to well water pumped was 69%.

TABLE 15

RADIUM REMOVAL IN ION EXCHANGE PLANTS

Plant	Ra in pCi/l	Ra out pCi/l	% Ra Rem.^{0}	TH in mg/lCaCO$_3$	TH out mg/lCaCO$_3$	% TH Rem.^{0}
Eldon, IA	49	1.9	96	375	10	97
Estherville, IA	5.7	0.3	95	915	46	95
Grinnell, IA	6.7	0.2	97	385	11	97
Holstein, IA	12	0.5	96	920	18	98
Dwight Corr. Inst., IL	3.26	0.36	89	286	43	85*
Herscher, IL	14.31	1.31	91	406	60	85*
Lynwood, IL	14.69	0.41	97	848	78	91
Sarasota, FL	4.3	0.70±	84	460	159±	65**

^{0} Removed

± Adjusted to take account of raw water blending.

* % hardness and % Ra removals are somewhat low due to breakthrough occurring prior to all samples being collected.

** % hardness and % Ra removals are somewhat low due to incomplete regeneration of media as 1/2 brine pumping capacity was down for repair.

Pretreatment of the feed water was necessary to prevent fouling of the membranes by suspended solids, iron, manganese and precipitated calcium carbonate and magnesium hydroxide.

Lime-Soda Ash Softening reached 95% radium removal efficiency. Considerable variations in radium removal were noted depending on chemical dosage, pH range, magnesium removal, non-carbonate hardness removal and filtration efficiency.

Bhagat (114) reported that, in the Austin Water Treatment Plant, the use of activated sludge removes 18 per cent of the radium in the feed (0.15± 1.71 p Ci per 1). The maximum amount of radium retained by the sludge was 2.15 p Ci per 1.

Finally, basic studies on the use of foam separation as a means of concentrating radium 226 was reported by Schoen (115). This technique is similar in many respects to flotation. Surface active agents capable of complexing radium are used. Air is passed through the solution and the radium concentrates in the foam fraction which is continuously removed.

Surface active reagents, tested on pure water solutions, included dodecy 1-benzyl-diethylene triamine tetraacetic acid, Igipon TC-42 (sodium N-methyl-N-"coconut oil acid" laurate and Aerosol 22 (tetrasodium N-(1,2-dicarboxyethyl) - N-octadecylsulfosuccinamate).

Concentration of radium in the foam fraction varied from 1 to 39. A marked dependence on pH and foaming agent concentration was demonstrated.

From the preceeding discussion it appears that;

- solvent extraction shows little promise as a means of removing radium 226 from either conventional or non-conventional uranium process effluents and liquors.
- reverse osmosis will reduce radium 226 to below 3 p Ci per 1 but produces a concentrate requiring further treatment.
- ion exchange shows the most promise for removing one or all of radium 226, thorium 230 and lead 210 from conventional uranium process effluents as well as from liquors produced from the non-conventional processing of uranium ores.
- For acid and carbonate process effluents, use of solid ion exchangers, either the synthetic zeolites or strong acid cation type exchangers, will reduce the level of the nuclides to environmentally acceptable levels.

- strong acid cation exchange resins can also be effective in removing the radionuclides from chloride, nitrate or EDTA, non-conventional process liquors if acid and total anion levels could be maintained to give effective extraction.

- if required, separation and purification of radium 226, thorium 230 and lead 210 may be acccomplished by proper choice of resins and eluting agents.

SECTION IV - SUMMARY OF CAPITAL AND OPERATING COSTS FOR RADIONUCLIDE CONTROL PROCESSES

Current practice for control of the environmental impact of liquid effluents from uranium milling operations is by neutralization, barium chloride treatment of tailings basin overflow, retention of precipitated barium radium sulfate in settling basins and discharge of settling basin overflow to natural watercourses.

Concern about precipitated barium radium sulfate contaminating natural watercourses by overflowing the settling basins has resulted in a target level of 10 p Ci per l total radium discharged to natural watercourses being set up by the Atomic Energy Control Board. Other concerns relate to the ultimate fate of radium in the sludge relative to its containment once the settling basins have reached their capacity and the potential for redissolving the precipitated radium. These latter concerns have resulted in the recent award of a contract by Energy Mines and Resources Canada, CANMET, to Kilborn Ltd. for the investigation of settling basin drainage followed by dredging of precipitated radium, dewatering, container storage of the sludge and ultimately burial underground. (59).

In light of the above, options for control were assessed in terms of their ability to remove the radionuclides, especially radium 226, in a form that is easily contained. This has led to the selection of ion exchange on barite, zeolites or strong acid resins as having the most promise as alternative control technology. The option of using strong acid ion exchange for control of radium 226, thorium 230 and lead 210 in nitric and hydrochloric acid uranium leach liquors appears to be technically feasible.

To assess the potential viability of these alternative control technologies, literature data on capital and operating costs, where available, have been summarized. A comparison is made with published cost data on barium chloride treatment of effluent.

It is not intended to draw any conclusions from the following discussion. Selected options have been tested in the laboratory under far from practical process conditions or have been used to treat waste water streams which differ substantially from mill process effluents or hypothesized leach liquors. In most cases cost data is incomplete but is reported so as to provide a complete record of the available literature.

IV.1 BARIUM CHLORIDE TREATMENT

Cost data on the use of barium chloride to control radium in conventional mill effluents is limited.

Consumption of barium chloride at Rio Algom's Quirke Mill and the Denison Mill are reported as 0.1 and 0.2 lbs. per 1,000 U.S. gal. (6). Reported cost for barium chloride is 15 cents per lb. (35) giving a chemical cost for treatment of between 1.5 and 3 cents per 1,000 U.S. gal.

Capital costs for settling basins and dam construction have not been published.

Given the potential requirement of intermittent drainage and drainage of settling basins along with the dewatering and bagging of sludge, added capital and operating costs will be incurred.

Iwata et. al. (54) published capital and operating cost data for the treatment of neutralized tailing dam overflow for radium 226 control. Tailing dam effluent from their pilot plant (260 to 1600 USGPM) is treated in agitated tanks with barium chloride (0.42 lbs per 1,000 U.S. gal.) bentonite (0.84 lbs per 1,000 U.S. gal.) and an unspecified precipitant (0.08 lbs per 100 U.S. gal.). The precipitated and coagulated barium radium sulfate is settled in 5 ponds whose total ares is 24,000 ft^2 and then filtered using 10 sand filters of total area of 10,000 ft^2 before discharge to receiving waters.

Capital cost of the radium removal facility is reported at $25,000.00.

Operating costs of 68.1 cents per 1,000 U.S. gal. are reported of which 22.5 cents are reagent costs. Of the remaining 45.6 cents, 26.6 cents was allocated to manpower, 15.0 cents to maintenance and 4.0 cents to electric power.

The reagent costs appear high given that, the cost for barium chloride and bentonite is calculated at 7.5 cents per 1,000 U.S. gal.

IV.2 ION EXCHANGE TECHNIQUES

The advantage of removing radionuclides from effluent streams and leach liquors by adsorption onto a solid matrix such as barite, zeolites or synthetic resins is that once adsorbed they can be contained in the equipment used to hold the ion exchange media. Thus, once loading efficiency has dropped sufficiently, the cylinder containing the radionuclides adsorbed on the solid exchanger or adsorbent can be disposed of intact or the matrix can be removed, dewatered bagged and then disposed of. If regeneration of the matrix was required, for economic reasons, the volume of liquor to be treated would be substantially reduced, facilitating its treatment and control of unwanted discharge.

Barite Treatment

Removal of radium 226 from conventional mill process tailings effluent has been proven in numerous pilot scale tests and was used in full scale operation at the Uravan Plant in the period 1958 to 1960.

Data in the literature (20, 25) does not permit a detailed economic assessment of barite decontamination of mill effluents. Barite consumption data is based on single column downflow adsorption of radium 226 and the mechanical loss of barite through the necessity of slime removal.

Reduced barite consumption could, most likely, be obtained by operating two or more barite ion exchange columns in series.

Slime build-up on the column, with the resultant increase in head pressure, necessitated the daily removal of slimes along with a portion of the barite bed. This difficulty can be alleviated by employing either continuous ion exchange principles with the barite in closed loop with the extraction column, or use of upflow ion exchange with slight bed expansion.

Operating at a downflow flowrate of 13.3 USGPM per ft^2 barite, consumptions of 4.15 lbs and 2.74 lbs per 1,000 U.S. gal. treated, were reported for reductions in soluble radium to averages of 3.7 and 5.9 p Ci per l respectively (20). Lower radium values could presumably be obtained employing the standard ion exchange procedures discussed above.

Comparing chemical costs for barite treatment with those for barium chloride precipitation of radium, use of barite would compare favourably if its consumption could be reduced to between 0.3 and 0.6 lbs. per 1,000 U.S. gal. Added costs not associated with barium chloride precipitation of radium would include, construction and maintenance of an ion exchange plant as well as grinding of barite.

Use of barite to remove radium from non-conventional chloride and nitrate leach liquor will be of limited utility. The high chloride and nitrate concentrations will probably result in dissolution of the barium sulfate.

Synthetic and Natural Zeolites

Preliminary studies previously,described (Section III), indicate that radium 226 would be effectively removed from neutralized tailings effluent by adsorption on a natural zeolite (clinoptilolite) or a synthetic zeolite (Decalso). Elution with 2 M ammonium nitrate was reported to regenerate both the clinoptilolite and Decalso to their original capacity.

More than 97 per cent of the radium was precipitated from the eluant as a granular rapidly settling solid by addition of 2.6 g ammonium sulfate and 5.2 barium nitrate per l eluant. The advantage of this method,as opposed to direct precipitation of barium sulfate from tailings pond effluent, is the concentration of radium in a small volume which is easy to store and treat.

No cost data were presented.

Given that high concentration of radium 226 in the feed (2200 to 2500 p Ci per 1) was used in the testwork, and that for this feed, adsorption was terminated when radium in the effluent reached 5 per cent of that in the feed, chemical costs were calculated for regeneration of the eluant.

With Decalso and Clinoptilolite the effluent activity was 5 per cent of the feed solution after passage of 6000 and 2000 column volumes respectively. Data presented on radium elution from clinoptilolite, with ammonium nitrate, shows that 20 column volumes are sufficient to desorb 97 per cent of the radium. This gives a volume of eluant to be treated of 10 U.S. gal. per 1,000 U.S. gal. tailings pond effluent treated by clinoptilolite. This translates to a chemical consumption of 0.22 lbs. ammonium sulfate and 0.43 lbs. barium nitrate per 1,000 U.S. gal. tailings effluent treated for a combined cost of 14.2 cents at current prices f.o.b. works (122).

If it can be demonstrated that for real solutions containing about 200 p Ci per 1 radium 226 adsorption can be extended by a factor of ten before regeneration was required, then the chemical costs would be in line with those reported for treating tailings effluent directly with barium chloride.

Presumably, the use of ammonium nitrate, sodium nitrate, ammonium chloride - hydrochloric acid or hydrochloric acid to elute radium from clinoptilolite would somewhat limit its use as an adsorbent for radium from chloride and possibly carbonate leach liquors. Some utility may be shown for radium removal from sodium nitrate liquors.

Strong Acid Ion Exchange

The use of strong acid cation exchange resins to remove the radionuclides, especially radium 226 from conventional uranium mill tailings effluent as well as nitrate and chloride liquors produced from non-conventional processing of uranium ore, is very promising.

As reported in the previous section of this report, use of water softeners in water treatment plants was effective in reducing feed radium 226 from 4.9 to 43 p Ci per l to a final level of less than 2 p Ci per l. Plant throughput varied from 200 to 1,000 USGPM. All plants used brine to regenerate the resin. Operating data are given below:

Operating exchange capacity equiv. per l.	0.92 - 1.60
Recommended bed depth, inches	24 - 48
Softening flow rate, gpm/sq.ft.	4 - 8
Softening flow rate, gpm/cu.ft.	2 - 6
Backwash flow rate, gpm/sq.ft.	5 - 6
Salt dosage, lbs/cu.ft.	5 - 20

Brine concentrations, %	8 - 16
Regeneration brine contact time, min.	24 - 45
Rinse flow rate, gpm/cu.ft.	
Slow	1 - 2
Fast	3 - 5
Rinse requirements gal/cu.ft.	20 - 40

Singley et. al. (121) estimated the capital, operating and maintenance costs for radium removal from potable water supplies by lime-soda softening, ion exchange and reverse osmosis.

For ion exchange, plant design and costs were based on blending of raw water with ion exchange column effluent to give a radium concentration in purified water of 5 p Ci per l. All cost data has as its basis, cost indices for October 1975.

A wide range of raw water quality, radium in raw water and population conditions were considered. Assumed total dissolved solids content, total hardness as calcium and radium 226 in the feed water assumed were in the range 400 to 2,000 ppm, 150 to 750 ppm and 7.5 to 50 p Ci per l respectively. Costs for brine regeneration of resin were included. Separate cost data were presented for various options for brine disposal including discharge to local receiving waters, evaporation, deep well injection etc.

The capital cost and annual operating costs of ion exchange softening plants for raw water radium concentrations of 20 and 50 p Ci per l are reproduced in Figures 19 to 22. These costs do not include the costs of ultimate disposal of regenerant brine solution.

It is readily seen that the capital and annual operating costs are strongly dependent on the hardness but not the radium content of the raw water. This is not surprising since, of the total exchange capacity of the resin, that portion utilized for radium loading is insignificant.

Capital cost for an ion exchange plant treating 1,000 USGPM and producing potable water from a feed having a total hardness as calcium carbonate of 759 ppm and radium in the range 20 to 50 p Ci per l would be $1,000,000.00. Annual operating costs of $104,000.00 to $108,000.00 or about 20 cents per 1,000 U.S. gal. would be incurred if brine regeneration were used.

Both the capital and operating costs of strong acid ion exchange could be substantially reduced if a greater fraction of the total exchange capacity of the resin can be utilized for radium removal to the exclusion of the other adsorbing cations.

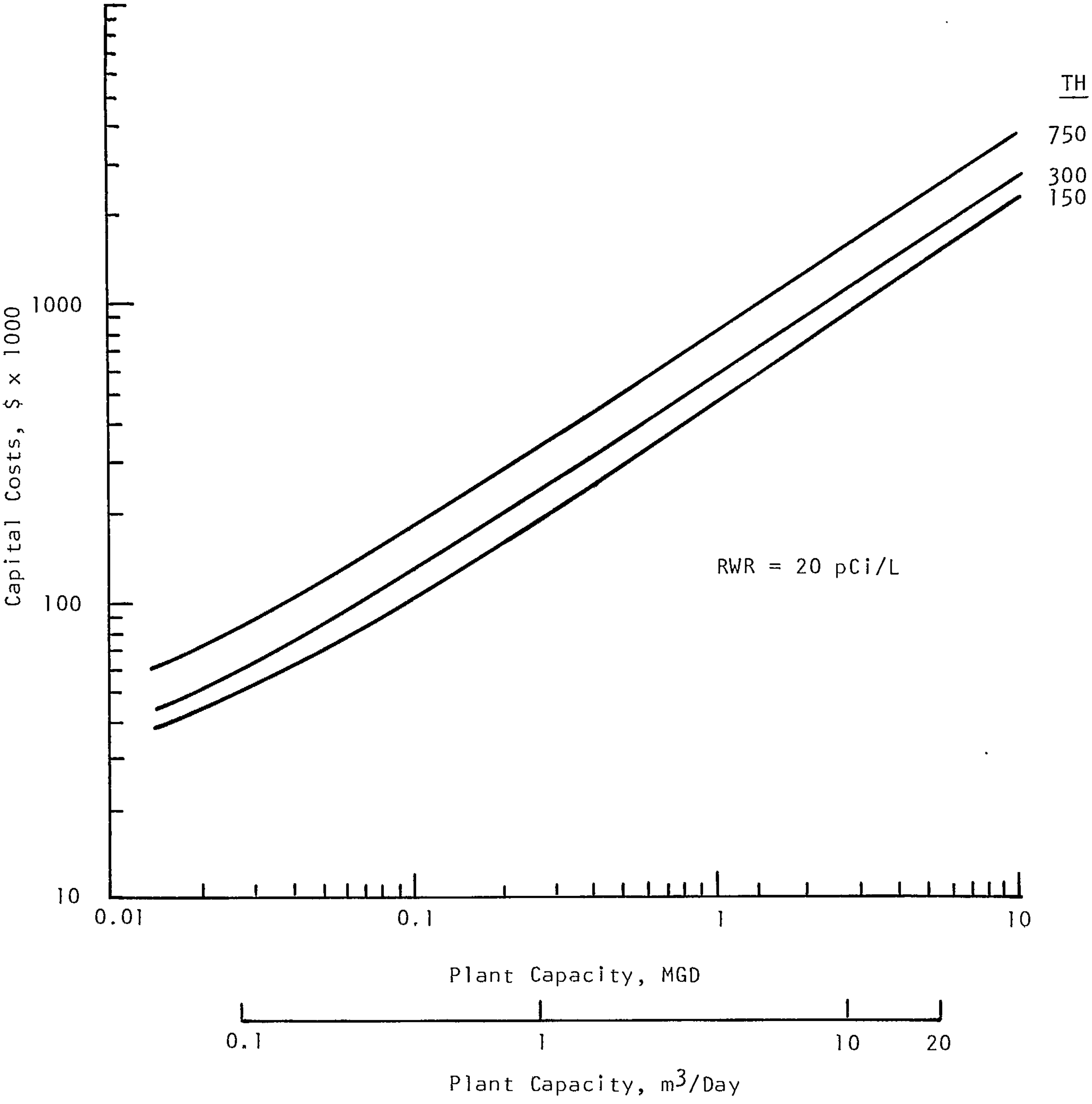


FIGURE 19

CAPITAL COSTS OF ION EXCHANGE PROCESS, RWR = 20 pCi/L

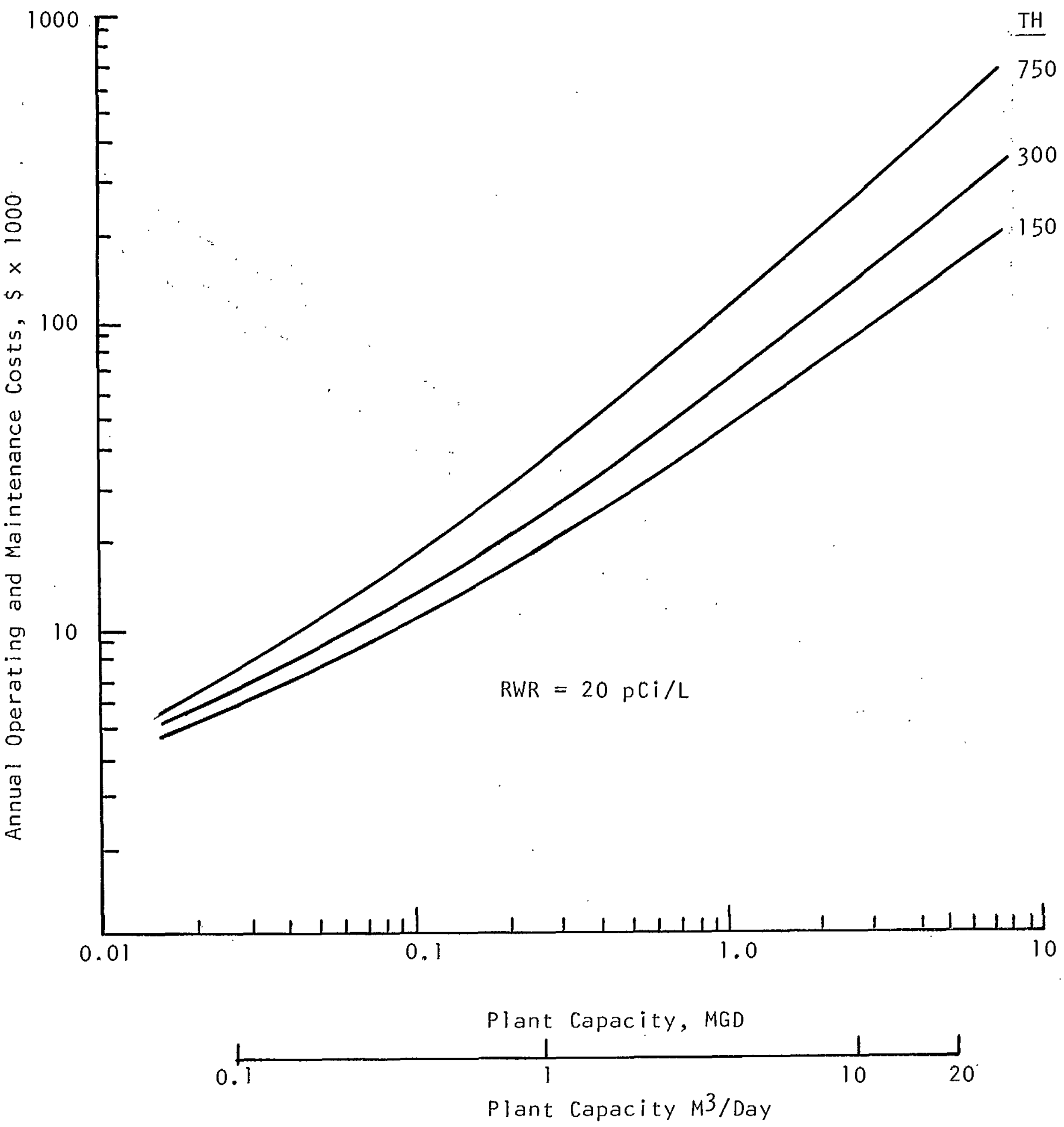


FIGURE 20

ANNUAL OPERATING AND MAINTENANCE COSTS OF ION EXCHANGE, RWR = 20 pCi/L

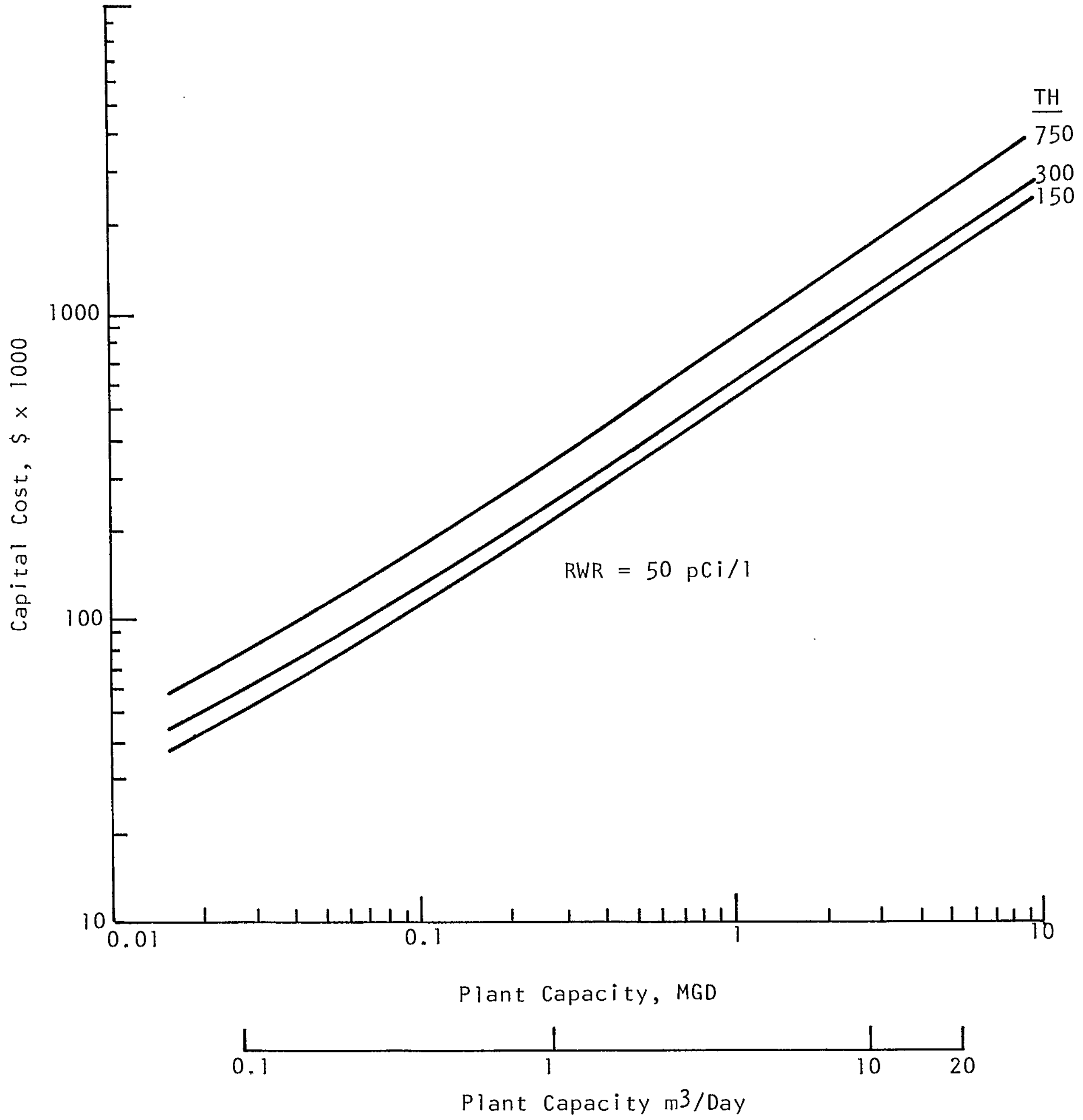


FIGURE 21

CAPITAL COSTS OF ION EXCHANGE PROCESS, RWR = 50 pCi/l

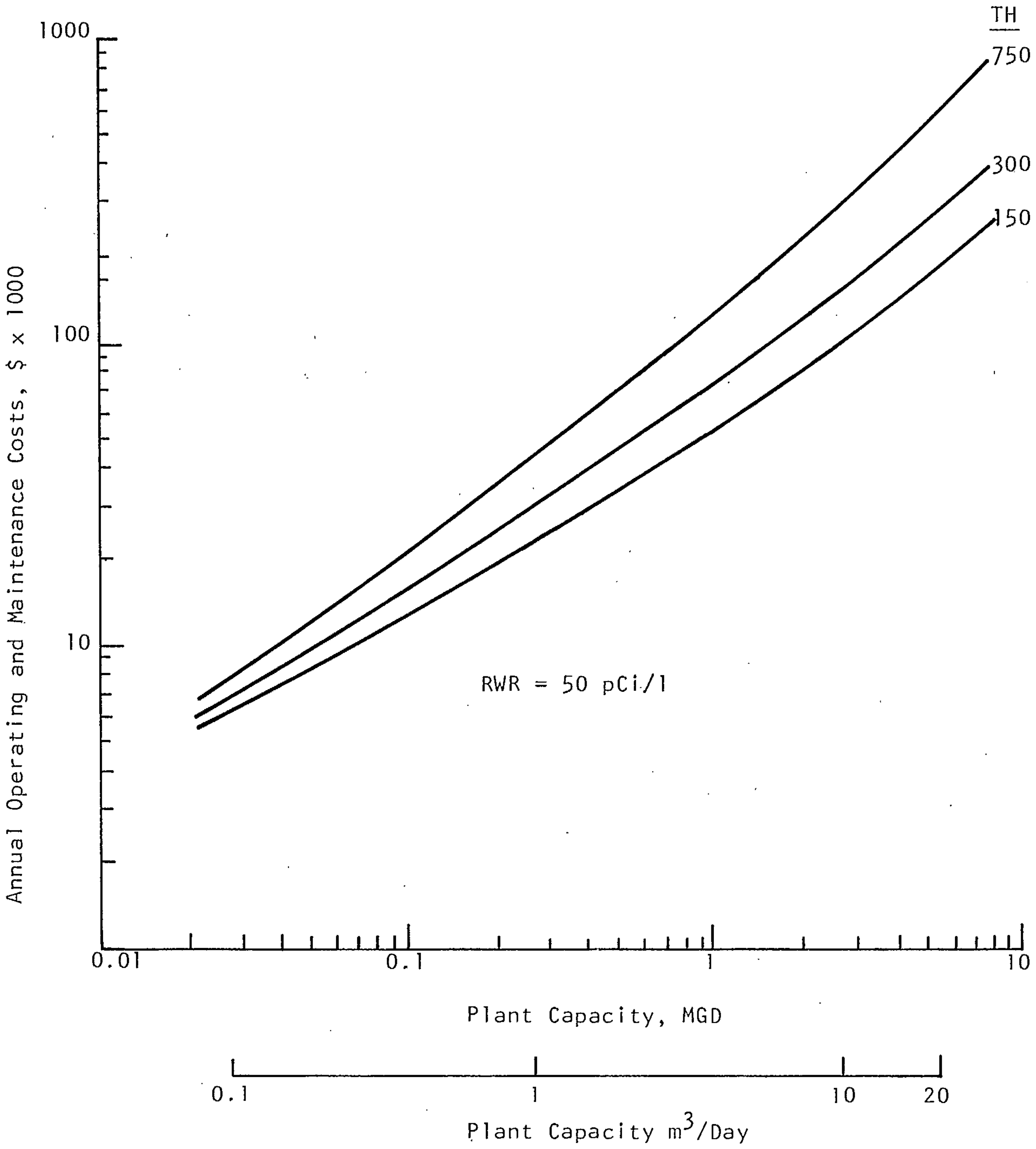


FIGURE 22

ANNUAL OPERATING AND MAINTENANCE COSTS OF ION EXCHANGE, RWR = 50 pCi/l

If sufficient radium can be adsorbed on the resin, disposal of the ion exchanger without the economic necessity of regeneration may be a viable option. The ultimate situation is where the total exchange capacity of the resin is utilized by radium. This scenerio is discusssed below.

Strong acid cation exchange resins have an operating capacity in the range 0.6 to 1.8 equivalents per l or a potential radium capacity of 113 g per l of resin. Assuming a radium level in neutralized tailings effluent from acid process mills of 200 p Ci per l, the theoretical loading of 1 liter of resin would require passage of 1.5×10^{11} U.S. gal. of effluent. It is improbable that anywhere close to this level of tailings pond effluent could be treated with this little resin even if radium loads to the exclusion of other cations, due to resin destruction by radiolysis.

Municipal water treatment plants employing ion exchange water softening as a means of radium 226 control have operated 10 per cent past normal regeneration times without adversely affecting the resins capacity for removing radium. What ultimate radium adsorption on strong acid cation exchange resins can be achieved from liquors containing high concentrations of other cations has yet to be determined.

SUMMARY

A critical assessment of published literature on the isolation of radium 226, thorium 230 and lead 210 from conventional uranium mill effluents and proposed alternate leachants for uranium ores is presented.

Conventional uranium ore milling based on sulfuric acid or carbonate leaching is described.

To assess the potential for radionuclide isolation during the milling process the distribution of radium 226, thorium 230 and lead 210 in milling circuits was reviewed. It was concluded that.

- In conventional milling of uranium ores radium 226 and thorium 230 are not dissolved to the same extent as uranium. Concentration procedures for uranium do not result in equal concentration of the dissolved radionuclides.

- Carbonate leaching of uranium ores dissolves significantly more radium 226 than does acid leaching. Significant quantities of thorium are dissolved in acid leaching whereas minor, if any, thorium is dissolved in carbonate leaching.

- Radium 226 dissolved in acid leaching appears to be re-precipitated or more probably adsorbed by cation exchange onto the fine clay minerals present in the slime fraction of

the solid tails. In alkaline leaching the same may be occurring.

- The processes used to recover uranium from acid leach liquors do not extract radium to any extent. The amount of thorium co-extracted with the uranium is marginal.
- The high radium 226 levels in the solids tailings discharged from both acid and alkaline milling, do not allow for long term surface storage.
- The high radium 226 content of plant liquid effluent associated with solids discharged, makes treatment mandatory before final discharge to natural watercourses.

Available literature data on the distribution of the radionuclides in both the solid and liquid fractions of conventional tailings ponds is reviewed. Data on leaching the radionuclides from solid tailings are presented. The data are discussed in terms of the proposed AECB target level for total radium 226 of 10 pCi per l and the Province of Ontario Guideline of 3 p Ci per l soluble radium 226 in mill discharge to natural watercourses. The following was concluded.

- The radium 226 content of the slime (-200 mesh) fraction is high enough that the AECB target for discharge of 10 p Ci per l total radium will be met, only if solids in the liquid tailings pond effluent is kept below 5 ppm.

- Control of soluble radium 226 by neutralization of the liquid tailings pond effluents does not reduce its concentration below the Province of Ontario Guideline.

- Limited data indicate that it is possible that lead 210 in liquid effluent from the tailings pond exceeds its maximum permissible concentration. Monitoring of tailings pond effluent for lead 210 should be required.

- The leaching characteristics of the radionuclides in solid tailings indicate that on mill shutdown, liquid effluent seepage and run-off from the tailings pile will have to be monitored and treated to meet the maximum permissible concentrations of the radionuclides of concern.

Studies leading to, and presently accepted treatment methods for, control of radium 226, thorium 230 and lead 210 in tailings effluents discharged to natural watercourses are reviewed. Recent testwork carried out to meet both the AECB target and Province of Ontario Guideline for total and soluble radium 226 discharged to natural watercourses is presented and discussed. Conclusions drawn include:

- Neutralization of acid mill effluents to pH 5 or higher adequately controls soluble thorium 230.

- No added treatment is required to control thorium 230 in carbonate mill effluents.

Of the options evaluated on pilot scale or employed in uranium mills precipitation of barium radium sulfate by controlled additions of barium chloride to acid mill tailings effluents or barium chloride and sulfate to carbonate mill tailings is the "Best Available Practical Technology." for control of radium 226 discharge.

- Levels of less than 3 p Ci per l soluble radium will be difficult if not impossible to achieve consistently using barium chloride treatment. A specification limit of 10 p Ci per l would appear realistic.

- The target level of 10 p Ci per l total radium in tailings effluent will not be attained using simple settling of barium radium sulfate. Use of flocculants appears to have promise. Discrepancies in the literature regarding the effectiveness of specific flocculants have to be resolved.

- Redissolution of precipitated barium radium sulfate poses a potential long term environmental problem. Many of the factors affecting the kinetics of redissolution need to be extensively studied.

- Alternatives to barium radium sulfate precipitation as a means of controlling radium need to be developed if the Provincial guideline of 3 p Ci per l soluble and the AECB target of 10 p Ci per l total radium discharged are to be met consistently. The alternative of radium adsorption onto barite shows promise and should be re-evaluated with the view to reducing barite consumption and meeting the above limits.

Alternate technology for the processing of uranium ore having the purpose of producing tailings low in radium, thorium and lead has been reviewed. The studies have been based on using chloride as a metal salt or acid, nitric acid or strong complexing agents as leachants. The processes along with proposed control procedures for the radionuclides are discussed and the following is concluded:

- Alternate uranium milling technology, to reduce the short and long term hazards associated with incomplete removal of radionuclides from tailings is in the early stage of development.

- The processes suggested by the early reported testwork are complex relative to existing technology.

- The corrosive nature of proposed leachants dictate a substantially higher capital cost relative to existing processes.

- The economic viability with respect to operating cost depend on almost total leachant recycle.

From a technical standpoint it is concluded that:

- A small but significant fraction of radium 226 in uranium ores is highly refractory and its dissolution is not achieved by the suggested processes. A lower level of about 50 p Ci per g radium 226 in final tailings appears practically attainable.

- Proven technology for the isolation of the radionuclides, especially radium 226, from the proposed leachants does not exist. The often mentioned use of sulfate and barium chloride to precipitate barium radium sulfate in isolation from the overall flowsheet is practical, but the build up of sulfate in recycled leachant will reduce leaching efficiency possibly to the point of making the process technically not feasible.

- Data must be generated, and the dissolution of thorium 230 and lead 210 by the proposed processes must be ensured for the long term resolution of the environmental problems associated with radionuclides in uranium extraction.

To provide alternatives for the recovery of the dissolved radionuclides from conventional mill tailings effluent and from chloride and nitrate containing leach liquors, a review of the chemistry of, and analytical procedures for, radium, thorium and lead was carried out.

Separation methods were analyzed and are reported.

Processes used to control the radium content in municipal water supplies were also reviewed and are presented.

Processes used to recover thorium from uranium mill residues as well as uranium refinery effluent control procedures were analyzed and pertinent information obtained is reported.

Conclusions arrived at with respect to alternative radionuclide control technology not based on either in-situ precipitation of barium radium sulfate or adsorption of radium onto barite include:

- Solvent extraction shows little promise as a means of removing radium 226 from either conventional or non-conventional uranium process effluents and liquors.

- Reverse osmosis will reduce radium 226 to below 3 p Ci per l but it produces a concentrate requiring further treatment.

- Ion exchange shows the most promise for removing one or all of radium 226, thorium 230 and lead 210 from conventional uranium process effluents as well as from leach liquors produced from the non-conventional processing of uranium ores.

- For acid and carbonate process effluents use of solid ion exchangers, zeolites or strong acid cation resins will probably reduce the level of the nuclides to environmentally acceptable levels.

- Strong acid cation exchange resins may also be effective in removing the radionuclides from chloride, nitrate or EDTA non-conventional process liquors if acid and total anion levels could be maintained to give effective extraction.

- Separation and purification of radium 226, thorium 230 and lead 210 may be accomplished by proper choice of resins and eluting agents.

A summary of published capital and operating costs for barium chloride treatment of conventional mill effluents for radium control and removal of radium 226 from liquid streams by ion exchange resins is presented. Available data are limited. No conclusions are drawn as the options selected have for the most part been tested in the laboratory under far from practical process conditions or have been used to treat wastes which differ substantially from mill process effluents or hypothesized alternate uranium process leach liquors.

SECTION V - REFERENCES

1. Griffith, J. W., "The Uranium Industry - Its History, Technology and Prospects," Mineral Report 12, Department of Energy Mines and Resources, Ottawa, (1967).

2. Williams, R. M. "Uranium Supply to 2,000, Canada and the World," Energy, Mines and Resources Canada, Bulletin MR-168, (1976).

3. Dakers, R. G., "Alkaline Leaching of Uranium Ores," in Extractive Metallurgy of Uranium - A Short Course, University of Toronto, May 29 - June 2, 1978.

4. Chambers, D. B., Knapp, R. A. and Gorber, D. M., "Perspectives for the Future," "Workshop on Radium 226 Control, Canadian Uranium Producers' Metallurgical Committee, 17th October, 1977.

5. Robert S. Kerr Environmental Research Laboratory, "State-of-the Art. Uranium Mining, Milling and Refining Industry," PB - 235 557, June 1974.

6. James F. MacLaren Ltd., "Environmental Assessment of the Proposed Elliot Lake Uranium Mines Expansion - Volume 1,Background Information, March 1977.

7. International Commission on Radiological Protection, ICRP Part II, "Report of Committee II on Permissible Dose for Internal Radiation," Pergamon Press, London, (1959).

8. Atomic Energy Control Board, "Summary Presentation," Workshop on Radium 226 Control, Canadian Uranium Producers' Metallurgical Committee, 17th October 1977.

9. Batelle Memorial Institute, "Program for the Management of Hazardous Wastes - Volume 1," PB -233 630, (1974).

10. Ritcey, G. M., "CANMET Research Pertaining to Ra^{226}," Energy, Mines and Resources Canada, ERP/MSL 77 - 287 (OP), September 1977.

10A. Skeaff, J.M., Unpublished data. Private communication, CANMET, Dept. Energy, Mines and Resources, Ottawa.

10B. Haque, K.E., "Hydrochloric Acid Leaching of an Elliot Lake Uranium Ore," CANMET, Ottawa, MSL-INT 78-66, 1978.

10C. Haque, K.E., "Second Stage Hydrochloric Acid Leaching of an Elliot Lake Uranium Ore - Preliminary Results," CANMET, Ottawa, MSL-INT 78-114, 1978.

11. Shearer, S. D., Sponagle, C. E., Jones, J. D., and Tsivuglou, E. C., Waste Characteristics for the Acid-Leach Solvent Extraction Uranium Refining Process. I. Gunnison Mining Company. Technical Report W62-17, "U.S.Public Health Service, R. A. Taft San. Engrg. Center, Cincinnati, Ohio 1962.

12. Cohen, J. B., Sponagle, C. E., Shaw, R. M., Jones, J. K., and Shearer, S. D., Waste Characteristics for the Acid-Leach Solvent Extraction Uranium Refining Process. II.Climax Uranium Company, Technical Report W62-17, U.S. Public Health Service, R. A. Taft San. Engrg. Center, Cincinnati, Ohio, 1962.

13. Cohen, J. B., Pahren, H. R., Lammering, M. W., Waste Characteristics for the Carbonate Leach Uranium Extraction Process. I. Homestake-New Mexico Partners Company, Technical Report W62-17, Cincinnati, Ohio, 1962.

14. Pahren, H.R., Lammering, M.W. Hernandez, Waste Characteristics for the Carbonate Leach Uranium Extraction Process. II. Homestake-Sapin Company, Technical Report W62-17, U.S. Public Health Service, R. A. Taft San. Engrg. Center, Cincinnati, Ohio. 1962.

15. Tsivoglou, E. C., Kalda, D. D., Dearwater, J. B., Waste Characteristics for the Resin-in-Pulp Uranium Extraction Process. Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Paper No. 2359, 21 pp. June 1958.

16. Merritt, R. C., " The Extractive Metallurgy of Uranium," Colorado School of Mines Research Institute, (1971).

17. Tsivoglou E. C. and O'Connell, R. L., Waste Guide for the Uranium Milling Industry," Tech. Rept., W 62-12, (1962).

18. Lendrum C., Personal Communication, (1976).

19. Shearer, S. D., "Waste Characteristics at Uranium Mills and Associated Environmental Aspects," Proceedings of the 11th Ontario Industrial Waste Conference, Toronto, (1964).

20. National Lead Co. Inc., "Topical Report January, 1960 - Summary Report on 1. The Control of Radium and Thorium in the Uranium Milling Industry, II. Radium 226 Analysis Principles Interference and Practice III. Current Winchester Laboratory Projects, "WIN-112, (1960).

21. Vivyurka, A. J., "The Pollution Control Program of Rio Algom Mines Limited in the Elliot Lake Region. Part II. Seepage Treatment and Control", Ontario Industrial Waste Conference Proceedings, 19, 85,(1972).

22. Vivurka, A. J., "The Pollution Control Program of Rio Algom Mines Limited in the Elliot Lake Region of Canada. Part II. Seepage Treatment and Control," Industrial Wastes, 22, (March/ April), 25, (1974).

23. Tsivoglou, E. C., and O'Connell, R. L., "Nature, Volume and Activity of Uranium Mill Wastes", Radiol. Health Safety Mining Nucl. Mater. Proc. Symp., Vienna, 2, 101, (1963).

24. Tsivoglou, E. C., "Environmental Monitoring in the Vicinity of Uranium Mills," Radiol. Health Safety Mining Milling Nucl. Mater. Proc. Symp., Vienna, 2, 231, (1963).

25. Misawa, H. et. al., "Solid and Liquid Wastes at the Ningyo-Toge Mine", Radiol. Health Safety Mining Milling Nucl. Mater. Proc. Symp., Vienna, 2, 123, (1963).

26. Beverly, R. G."Waste Management in Mining and Milling of Uranium," Radiation Protection in Mining and Milling of Uranium and Thorium. Proceedings of a Symposium, 301, (1974).

27. National Lead Company Inc., " Summary Report, 1959 - 1961 Winchester Laboratory," TID, WIN 125, September 30, 1961.

28. National Lead Company Inc., "Interim Report on Investigations into the problem of Radioactive pollution of Uranium Mill Effluents," WIN - 101, (1958).

29. Nuclear Regulatory Commission, "The Operation of Humeca Uranium Mill, Rio Algom Corporation. Docket Number 40 - 8084," PB - 251 929, (April 1976).

30. Chardon, P., and Kremer, M., "Handling of Solid and Liquid Wastes from the Bois-Noirs Mine-Plant Complex of the Forez Division: Purification of Effluents," Radiol. Health Safety Mining Milling Nucl. Mater. Proc., Symposium, Vienna, <u>2</u>, 155, (1963).

31. Beverly, R. G., "Disposal of Radioactive Waste from the Operation of Uranium Mills and Mines," Nuclear Safety, <u>6</u>, (3), 280, (1965).

32. Beverly, R. G. "Summary of Presentation on Radium and Thorium Behaviour in Uranium Milling Circuits - Statement of Air and Water Concentration Limits Prescribed in Part "20", Symposium on Radiochemical Problems in Uranium Milling, Colorado, October, 1960.

33. Clifford A. E., "Inorganic Chemistry of Qualitative Analysis," Prentice Hall, New Jersey, (1961).

34. Lakshmanan V. I. and Ashbrook A. W., "Radium Balance Studies at the Beaverlodge Mill of Eldorado Nuclear Limited," Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alberquerque, New Mexico, NEA/OECO, 24 - 28 July, 1978.

35. E. Larogue, Denison Mines Ltd., Personal Communication, (1978).

35a. Ryon, A. D., Hurst F. J. and Seeley F. G., "Nitric Acid Leaching of Radium and Other Significant Radionuclides from Uranium Ores and Tailings," ORNL/TM-5944, (1977).

36. Borrowman, S. R., and Brooks, P.T., "Radium Removal from Uranium Ores and Mill Tailings," Bureau of Mines RI 8099, 1975).

37. Seeley, F. G., "Problems in the Separation of Radium from Uranium Ore Tailings," Hydrometallurgy, 2, 249, (1976)/1977)

37A. Silver, M. and Andersen, J.E., Unpublished data, CANMET, Ottawa.

37B. Joe, E.G., Private communication, Unpublished data, CANMET, Ottawa.

37C. Skeaff, J.M., Private communication, Unpublished data, CANMET, Ottawa.

38. Sears, M. B., Blanco, R. E., Daniman, R.C., Hill, G. S. Ryon, A. D. and Witherspoon, J. P., "Correlation of radioactive waste treatment costs and the environmental impact of waste effluents in the nuclear fuel cycle for use in establishing "as low as practicable" guides-milling of uranium ores," ORNL-TM-4903, Vol. 1, (1975).

39. Moffett, D., Zahary, G., Campbell, M.C. and Ingles, J.C., "CANMET'S Environmental and Process Research on Uranium," Energy Mines and Resources, CANMET Report 77-53, July 1977.

40. Shearer Jr. S. D., and Lee, G. F., "Leachability of Radium 226 from Uranium Mill Solids and River Sediments, "Health Physics, 10, 217 (1964).

41. Shearer Jr. S. D., "The Leachability of Radium 226 from Uranium Mill Waste Solids and River Sediments, "Ph. D. Thesis, University of Wisconsin, (1962).

42. Havalik, B., Grafova, J., and Nycova, B., "Radium 226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - 1.The Effect of Different pH of Surface Waters," Health Physics, 14,417, (1968).

43. Havilik, B., Nycova, B. and Grafova, J., "Radium 226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - II. The Effect of Different Chemical Composition of Surface Water," Health Physics, 14, 423, (1968).

44. Wiles, D. R., "The Leaching of Radium from Beaverlodge Tailings," Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alburquerque, N. Mexico NEA/OECO, July 1978.

45. Levins, D. M., Ryan R. K. and Strong K. P., "Leaching of Radium from Uranium Tailings," Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alberquerque, New Mexico, NEA/OECO, 24 - 28 July, 1978.

46. Schmidtke, N. W., Averil, D., Bryant, D. N., Wilkinson, P., and Schmidt, J.W., "Removal of Radium 226 from Tailings Pond Effluents and Stabilization of Uranium Mine Tailings - Bench and Pilot Scale Studies," Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alberquerque, New Mexico NEA/OECO, 24 - 28 July, 1978.

46A. Ritcey, G.M., Silver, M., McCready, R.G.L. and Rolko, V.M., "Effect of Bacteria and Organics on Elliot Lake Tailings," Progress Report, MSL-INT 78-104, 1978.

47. Foster, R. F., "Sources and Inventory of Radioactivity in the Aquatic Environment," Batelle Northwestern, BNWL-SA-4614, June 1973.

48. Yourt, G. R., "Radiological Control of Uranium Mine and Mill Wastes, "Proceedings of the 13th Conference on Industrial Waste, 107, (1966).

49. Lakshmanan V. I., Macdonald, D. E., and Ashbrook, A. W., "Radium Control Studies in Eldorado," CUPMC Workshop on Radium Control, October, 1977.

50. Perez Pera C., Iranzo Gonzalez E. and y Lara Suenz D., "Treatment and Handling of Radioactive Wastes in the Andujar Uranium Mill," JEN - 108 - DMA - 1 - 15, (1963).

51. National Lead Company Inc., Quarterly Report, October 1, 1960 - December 31, 1960," WIN - 121, TID - 4500, February, 1961.

52. Curie, P. and Curie, M., "Sur une substance nouvelle radio-active, contenue dans la pechblende", C.R. Acad Sci. Paris, 127, 175, (1898).

53. Kuebel, A., "Extraction of Radium from Canadian Pitchblende," J. of Chemical Education," 17, 417, (1940).

54. Iwata, I., Kitchara, Y., Takenaka, S. and Kurokawa, Y., "Mill Tailings Disposal and Environmental Monitoring at the Ningyo - Toge Uranium Processing Pilot Plant," Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alburquerque, New Mexico, NEA/OECD, 24 - 28 July, 1978.

55. Moffett, D. and Vivyurka, A. J., "Control of Radium 226 Releases in Liquid Effluents, "Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Alburquerque, New Mexico, NEO/OECD, 24 - 28 July, 1978.

56. Kremer, M., "Method of Separation of Radium," Canadian Patent No. 778,831, Feb. 20, 1968.

57. Fournier P. M., "Current Research and Development on Radium 226 Control at the French Atomic Energy Commission," CUPMC Workshops on Radium 226 Control, October 1977.

58. Wilkinson, P. and Cohen, D.B., "The Optimization of Filtered and Unfiltered Ra 226 Removal from Uranium Mining Effluents - Status Report (1976 - 1977),"CUPMC Workshop on Radium 226 Control, October, 1977.

59. Supply and Services Canada, Research and Development Bulletin, 69, December 1978.

60. Goldsmith, W. A. Haywood, F. F., and Jacobs, D. G., "Guidelines for Cleanup of Uranium Tailings from Inactive Mills,"Conf.-760202-3, (1975).

60A. Raiceivc, D., "Decontamination of Elliot Lake Uranium Tailings," presented at Conference of Metallurgists, CIM, Montreal, August, 1978.

61. Riordan, M. C., M. J. Duggan, W. B. Rose, and G. F. Bradford. The Radiological Implications of Using By-Product Gypsum as a Building Material. National Radiological Protection Board (England), 1972, 24 pp.

62. Afanasev, M. K., and E. M. Krisyuk. Standards for Natural Radioactive Substances in Building Materials. Leningrad Res. Inst. of Radiation Hygiene (U.S.S.R.), 1973, pp. 387-391.

63. Sawyer, C., Wand Handley, R. W., "Process of Extracting Uranium and Radium from Ores," U.S.Patent No. 2,894,804, 14 July 1959.

63A. Skeaff, J.M., "Chlorination of Uranium Ore for Extraction of Uranium, Other Radionuclides and for Pyrite Removal," Presented at CIM Conference of Metallurgists, August, 1978. Accepted for Publication in CIM Bulletin.

64. Ryan, A. D. and Blanco, R. E., "Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle for Use in Establishing "As Low as Practicable" Guides - Appendix A. Preparation of Cost Estimates for Volume 1, Milling of Uranium Ores," ORNL - TM - 4903 Vol. 2., May 1965.

65. Sedlet, J., "Radon and Radium," Treatise on Analytical Chemistry, Part II, Vol. 4, 219, (1961).

66. Bonner, N. A., and Kahn, M., "Behaviour of Carrier Free Tracers," Radioactivity Applied to Chemistry, Wiley, New York, 1951.

67. Hahn, O., "Applied Radiochemistry," Cornell University Press, Ithaca, New York, 1936.

68. Grimaldi, F. S., "Thorium," Treatise on Analytical Chemistry, Part II, 5, 139, (1961).

69. Brodsky, M. Sartorius, R., and Sousselier, Y., "Production of Thorium Nitrate from Uranothorianite Ores," Progress in Nuclear Energy, Series III, Process Chemistry, 2, 68, (1958).

70. Van Cleave, A. B., and Baerg, A. P., "The Extraction of Th 230 (Ionium) from a Canadian Pitchblende Residue, Canad. J. Tech., 34, 425,(1957).

71. Carswell, D. J.,Fletcher, J. M., and Clelland, D. W., "The Recovery of Thorium 230 from Uranium Wastes," J. Inorg. Nucl. Chem. 5, 147, (1957).

72. Peppard, D. F., et. al., "Studies of the Solvent Extraction Behaviour of the Transition Elements. II. Isolation of Gram Quantities of Th 230 (Ionium) from a Pitchblende Residue," J. Amer. Chem. Soc., 75, 4576, (1953).

73. Perkins, R.W., and Kalkward, D.R., "Determination of Thorium in Urine", Anal. Chem., 28, 1989, (1956).

74. Gilbert, Jr., T.W., "Lead", Treatise on Analytical Chemistry, Part II, 6, 69, (1964).

75. Craig, D.N. and Vinal, G.W., "Solubility of Lead Sulfate in Sulfuric Acid Determined by Dithiozone with a Photronic Cell", J. Res. Natl. Bur. Std., 22, 55, (1939).

76. Willard, H.H., and Goodspeed, E.W., "Separation of Strontium, Barium and Lead from Calcium and Other Metals by Precipitation as Nitrates", Ind. Eng. Chem., Anal. Ed., 8 414, (1936).

77. Kallmann, S., "Determination of Lead as Chloride, Separation from Bismuth and Other Elements", Anal. Chem., 23, 1291, (1951).

78. De, A. K., Khopkar, S. M., and Chalmers, R. A., "Solvent Extraction of Metals," Von Nostrand Reinhold Co., 1970.

79. Carswell, and Fletcher, J. M., "The Recovery of Thorium 230" Progress in Nuclear Energy, Series III, Process Chemistry, 2, 80, (1958).

80. Boback M. W., Davis, J.O., Ross, K.N., and Stevenson J. B., "Disposal of Low-Level Radioactive Wastes from Pilot Plants," Chemical Engineering Progress, 67 (4), 81, (1971).

81. Iowa Dept. of Environmental Quality, Des Moines, "Determination of Radium Removal Efficiencies in Iowa Water Supply Treatment Processes," PB-259 509. (April 1976).

82. Athvale, V. T., Parekh, P.P., and Sunkar Das M., "Studies on Radioactive Disequilibrium of Certain Uranium Bearing Ores of India: Part 1 - Isolation and Estimation of Uranium and Its Daughter Products," Indian J. Chem., 6 206, (1968).

83. Marcus, Y., "Metal Chloride Complexes Studied by Ion Exchange and Solvent Extraction Methods, IA - 1087, December 1966.

84. Longchambon, M. L., "Procede de Recuperation et de Concentration du Radium," French Patent, 679,086, 3 December, 1928.

85. Linder, R., "Die Abtrennung des Bariums vom Radium durch radio-metrische Adsorptionsanalyse. (Das Verhalten der Radium-Emanation)", Naturwiss., 33, 119, (1946).

86. Stern, H., German Patent, 280694, 1914.

87. Arnold, W. D., and Crouse, D. I., "Radium Removal from Uranium Mill Effluents," I and E C Process Design and Development, 4, 333, (1965).

88. A. H. Ross & Associates, "Radium in Australian Mill Effluents - An Extract from the Ranger Environmental Inquiry Report," CUPMC Workshop on Radium 226 Control, October 1977.

89. National Lead Company Inc., "Winchester Laboratory, Quarterly Report, April 1, 1960 - June 30, 1960," WIN-117 TID-4500, August 26, 1960.

90. Karalova, Z. K., Shivaeva, N.P., and Pyzhova, Z. I., "An Express Method for Separating Ionium (Th^{230}) from Sulfuric Acid solutions of Uranium, "Zhurnal Analiticheskoi Khimu, 21, 950, (August, 1966).

91. Karalova, Z. K. and Pyzhova, Z. I., "An Ion-Exchange Concentration of Thorium Isotopes with Similtaneous Separation from Uranium," Zhurnal Analiticheskoi Khimu ,23 , 940, (June 1968).

92. Tame, K.E., and Rosenbaum, J. B., "Disposal of Liquid Waste in the Resin - In Pulp Type Uranium Milling Flowsheet," Bu Mines R1 6114, (1962).

93. Khopkar, S.M., and De, A.K., "Cation Exchange Studies of Pb^{II} on Dowex 50 - WX8", Talanta 7, (1960).

94. Ichikawa, F., Uruno, S. and Imai, H., "Distribution of Various Elements between Nitric Acid and Anion Exchange Resins", Bull. Chem. Soc. Japan, 34, 952, (1961).

95. Tompkins, E.R., "Separation of Radium from Barium", U.S. Patent No. 2,554,649, 29th May, 1951.

96. Hagemann, F., "Isolation of Actinium", J. Am. Chem. Soc. 72, 768, (1950).

97. Bush, W.E., and Higgins, L.J., "Handbook of Analytical Proceedings, Supplement to RMO 3001, Rev. No. 1", T10 - 4500 June 17, 1965.

98. Carswell, D.J., "Separation of Thorium and Uranium Nitrates by Anion Exchange", Inorg. & Nucl. Chem., 3, 384, (1957).

99. Dai, M.H., Lu, W.D. and Wu, S.C., "Application of a Pretreated Straw Column to the Separation of Thorium and Uranium", Separation Science, 11, 541, (1976).

100. Nelson, F. and Kraus, K.A., "Anion Exchange Studies XI: Pb^{II} and Bi^{III} in Chloride and Nitrate Solutions", J. Am. Chem. Soc., 76, 5916, (1954).

101. Kraus, K.A. and Nelson, F., "Anion Exchange Studies of the Fission Products", Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 7, 113, (1956).

102. Diamond, R.M., "Factors Influencing Ion-Exchange Equilibria in Concentrated Solutions: Behaviour of the Alkaline Earth and Alkali Ions", J. Amer. Chem. Soc. 77, 2978, (1955).

103. O'Janne, L., "Research in Radiochemistry, Progress Report for year ending January 31, 1961", U.S. Atomic Energy Commission, TID-11815, (1961).

104. Germann, F.E.E., "Adsorption of Radium by Barium Sulfate", J. Amer. Chem. Soc., 43, 1615, (1921).

105. Kraus, K.A., Moore, G.E., and Nelson, F., "Anion Exchange Studies XXI: Th^{IV} and U^{IV} in HCl Solutions. Separation of Th, Pa and U", J. Am. Chem. Soc., 78, 2692, (1956).

106. Petrow, H.G., Nietzel, O.A. and De Sesa, M.A., "Radiochemical Determination of Radium in Uranium Milling Process Samples", Analytical Chemistry, 32, 926, (1960).

107. Yoshina, Y. and Kojima, M., Japan Analyst, 6, 160, (1957).

108. Strelow, F.W.E., "An Ion Exchange Selectivity Scale of Cations Based on Equilibrium Distribution Coefficients", Anal. Chem., 32, 1185, (1960).

109. Kellex Corporation, "Recovery of Ra from U Ore Acid Leach Residues - Progress Report for the Period May 1 - 31, 1950, "KLX - 1203, (1950).

110. Kozak, M. A., Baczuk, B. J. and Landram, G. K., "GET THE LEAD OUT Methods For Removing Lead from Plant Waste Water Streams," SUN 143 - 10, 2 August,1971.

111. Singley, J. E., Beaudet, B. A., Bolch, W. E., and Palmer, J. F., "Costs Of Radium Removal from Potable Water Supplies," PB - 226 950, (April 1977)

112. Vermeulen, L. W., "Recovery of Thorium from Uranium Solutions," Journal of Metals, 23, January 1966.

113. Petrow, H. G. and Lindstrom, R., "Radiochemical Determination of Radium in Uranium Milling Process Samples," Analytical Chemistry, 33, 313, (1961).

114. Bhagat, S. K., and Gloyna, E. F., "Environmental Radionuclides in Muncipal Wastewater," Water and Sewage Works 110, (5), 205, (1963).

115. Schoen, H, M., Rubin, E. and Ghosh, D., "Radium Removal from Uranium Mill Wastewater," J. Water Pollution Control Federation, 34, 1026, (1962).

116. Bagnall, K. W., "Chemistry of the Rare Radio elements," Butterworths Scientific Publications, London, 1957, pp 131 - 149.

117. Erbacher, O., "Solubility of Radium Salts", Ber., 63B, 141, (1930).

118. "Stability Constants of Metal Ion Complexes," Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971.

119. Gayer, K.H., and Leider, H., "Solubility of Thorium Hydroxide in Solution of Sodium Hydroxide and Perchloric Acid at 25°", Am. Chem. Soc., 76, 5938, (1954).

120. Clifford, A.F., "Inorganic Chemistry of Qualitative Analysis", Prentice-Hall Inc., New Jersey, 1961.

121. Singley, J. E., Beaudet, B. A., Bolch, W. E., and Palmer, J. F., "Costs Of Radium Removal from Potable Water Supplies," PB - 226 950, (April 1977).

122. Chemical Marketing Reporter, December 4, 1978.

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