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THE DISPOSAL OF SOLID WASTES AND LIQUID EFFLUENTS FROM THE MILLING OF URANIUM ORES

D. Moffett

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The Disposal of Solid Wastes and Liquid Effluents from the Milling of Uranium Ores

by

D. Moffett*

ABSTRACT

Current Canadian practice in the milling of uranium-bearing ores commonly involves fine grinding followed by acid leach/ion exchange. The acid leach may be followed instead by solvent extraction. Alkaline leaching has been done, and in situ bacteriological leaching is of interest.

Tailings disposal operations are necessary and create environmental problems. Uranium-mill wastes are unique because of their radioactivity. Some of the radioisotopes present may require an individual control procedure. Radium-226 is particularly important because it is the most hazardous of all isotopes found in the tailings. Acid and heavy-metal removal is conventionally done by the addition of lime, but other means are available, such as with limestone, sodium hydroxide, ammonia, silicon alloys or by sulphide precipitation.

Modifications to unit operations in the mill process may be required to produce more acceptable effluents. Increased water recycling may be necessary to meet regulatory standards.

Key words: Uranium, Tailing Disposal, Effluent Control, Radium-226, Water Treatment.

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L'évacuation des résidus solides et des effluents liquides provenant du broyage de minerais d'uranium

par

D. Moffett*

RESUME

La façon la plus courante de broyer des minerais porteurs d'uranium au Canada, consiste en un broyage fin suivi de lixiviation acide et d'un échange d'ions. On peut également procéder à l'extraction au solvant après la lixiviation acide. La lixiviation alkaline a aussi été mise à l'essai et la lixiviation bactériologique in-situ s'est avérée assez intéressante.

Malgré les problèmes environnementaux qu'elles posent, les méthodes d'évacuation des résidus sont nécessaires. Mais les rejets d'uranium ont quelque chose de particulier et c'est leur radioactivité. Certains des radioisotopes présents pourraient avoir besoin d'un moyen de contrôle approprié. Le radium-226 est le plus dangereux des isotopes trouvés dans les regets. L'extraction de l'acide et des métaux lourds est traditionnellement effectuée par l'addition de chaux, ou encore de calcaire, d'hydrate de sodium, d'ammoniaque, d'alliages de silicone ou par précipitation au sulfure.

On devra peut-être modifier certaines opérations du broyage afin de produire des effluents qui soient moins dommageables à l'environnement. Et une plus forte proportion d'eau à recycler devra probablement être atteinte afin d'être conforme aux normes.

Mots clefs: Uranium, évacuation des résidus, contrôle des effluents, radium-226, traitement à l'eau.

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1. URANIUM EXTRACTION IN CANADA

1.1. Introduction

Canada is presently the world's second largest producer of uranium with a total production of 4400 tonnes* U_3O_8 in 1975 (1). The increasing demand for uranium requires the mining of lower-grade ores and more and larger mining and milling operations. The processing of uranium ore results in the need to dispose of large quantities of solid wastes and liquid effluents. Since the ore contains as little as 0.85 kg U_3O_8 per tonne, the waste volume often exceeds 99% of that of the ore mined. Furthermore, the radioactive nature of this waste necessitates its containment and control. A list of active uranium mines is shown in Table 1.1. with ore grades and extraction methods. The major producing area of Canada is the Elliot Lake region of Ontario. Here the total amount of solid waste already deposited is about 80 million tonnes. The principal uranium mining areas of Canada are shown in Fig. 1.1.

Tailings are commonly pumped into a natural lake, basin or swamp where the solid portion may be contained by a dam. The liquid effluent is allowed to decant and discharge into the nearest watercourse. This practice has resulted in serious impairment of the water quality and

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* Metric tons.

TABLE 1.1

Current Canadian Practice in the Milling of Uranium Ores, 1975

Company and Milling Capacity (tonnes/day)[a]	Location	Ore Grade (kg/tonne)	Extraction Process
Agnew Lake Mines[b]	Agnew Lake, Ont.	0.83	In situ bacteriological leach/ion exchange
Amok (100)[c]	Cluff Lake, Sask.	9.44	Preconcentration/ acid leach
Denison Mines (6500)	Elliot Lake, Ont.	0.96	Acid leach/ion exchange
Eldorado Nuclear (900)	Beaverlodge, Sask.	2.82	Alkaline leach
Gulf Minerals (1300)	Wollaston Lake, Sask.	3.74	Acid leach/solvent extraction
Madawaska Mines (1500)[d]	Bancroft, Ont.	1.04	Acid leach/ion exchange
Rio Algom, Quirke (4000)	Elliot Lake, Ont.	1.40	Acid leach/ion exchange

a - Some mills have not reached designed capacity.

b - No figure available but estimated production in 1978 - 450,000 kg U_30_8.

c - Operational - late 1978.

d - Operational - late 1976.

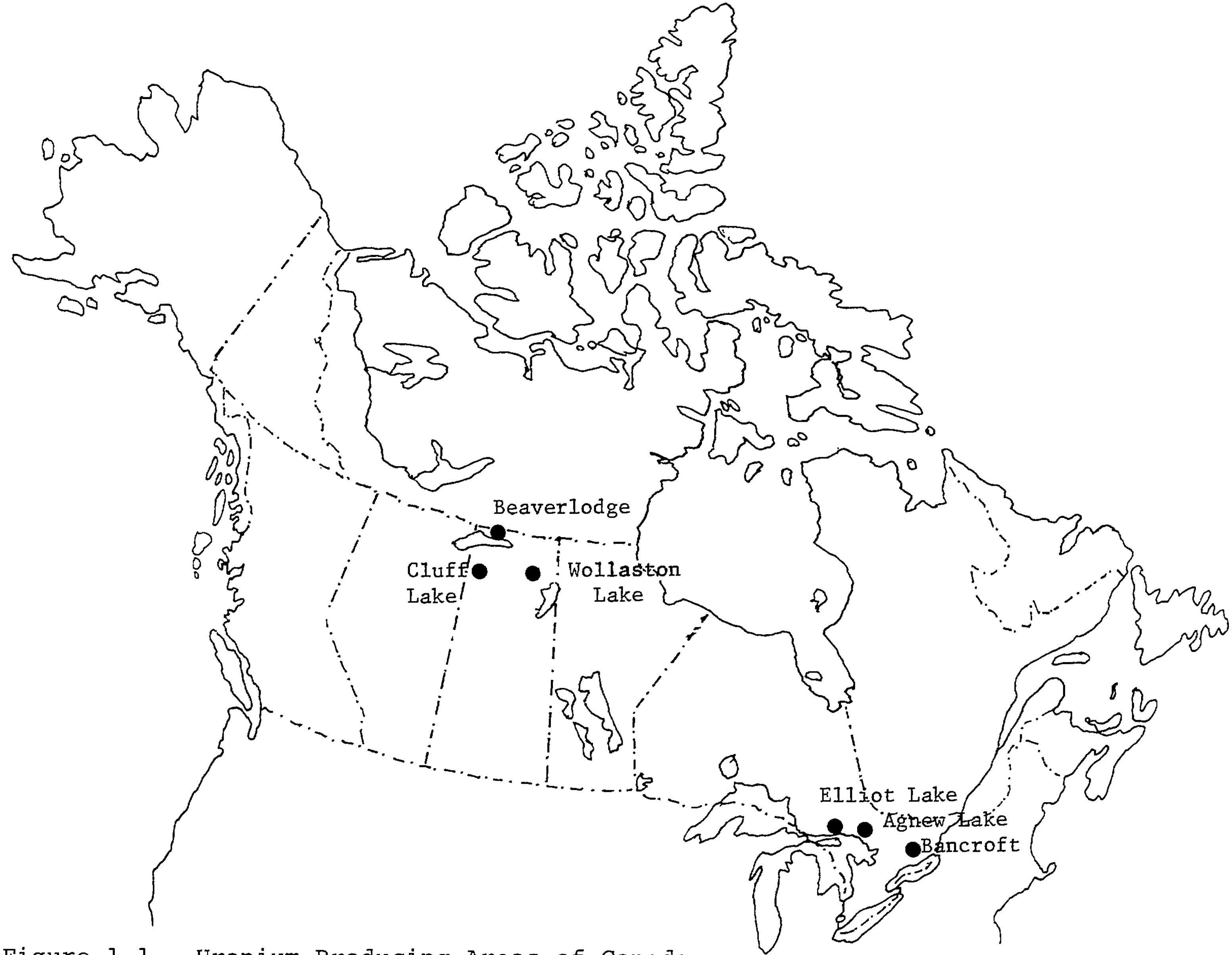

Figure 1.1. Uranium Producing Areas of Canada

its effect on plant and animal life - one example being the Serpent River Basin (2). More stringent control measures are currently being enforced.

One of the objectives of the Department of Energy, Mines and Resources is to ensure effective use of the mineral resources available to Canada. However, it is recognised that this is subject to environmental constraints and it is necessary to minimize the adverse effects of tailings disposal on the surface environment and to restore land to aesthetically acceptable standards.

This report reviews both past and present disposal practice; emphasis is placed on the various means available to the uranium mining industry for reducing pollution.

1. 2. The Milling of Uranium Ores

The goal of the industry is a product containing about 80% U_30_8 (yellowcake) from ores whose average grade may be less than 0. 15% U_30_8. Hydrometallurgical milling may be achieved by either an acid or alkaline leaching process depending upon the physical and chemical characteristics of the ore. The operating mills are listed in Table 1. 1. and this table reveals the widespread use of sulphuric acid leaching for the extraction of uranium from Canadian ores.

1. 2. 1. The Acid-leach Process

Acid leaching of a uranium ore is most often accomplished with hot sulphuric acid. Air or sodium chlorate is used as an oxidant which, with the iron in the ore, ensures that all the dissolved uranium is in the hexavalent state.

A typical acid-leach flowsheet is shown in Fig. 1. 2. The uranium is dissolved from the ore, and following a partial neutralization, the solution is separated from the barren solids. The uranium-containing solution is then clarified and passed to the extraction circuit. Here the leach-liquor must first be upgraded either by ion exchange (IX) or solvent extraction (SX) to produce a final solution from which the yellowcake may be precipitated. Both methods involve the preferential complexation of the uranium species by absorption onto an IX resin or extraction into an organic solvent. Finally, the uranium-rich solution can be eluted from the resin or solvent, by nitric acid for example, and the yellowcake can be precipitated from this solution by ammonia. The barren solution is combined with the leached and washed solids and, after neutralization with lime or limestone, is discharged as tailings.

The acid leach dissolves considerable quantities of impurities from the ore in addition to the uranium but these are reduced to low concentrations by neutralizing the tailings. Process waste also contains the highly soluble reagents added in the milling. Table 1. 2 lists the reagents and materials used in the milling of one tonne of uranium-bearing ore. Only the ammonia is present in the final yellowcake concentrate as ammonium diuranate $(NH_4)_2U_2O_7$ and all of the other reagents listed in Table 1. 2 are discharged in the tailings and constitute a major contribution to the pollution load on the environment.

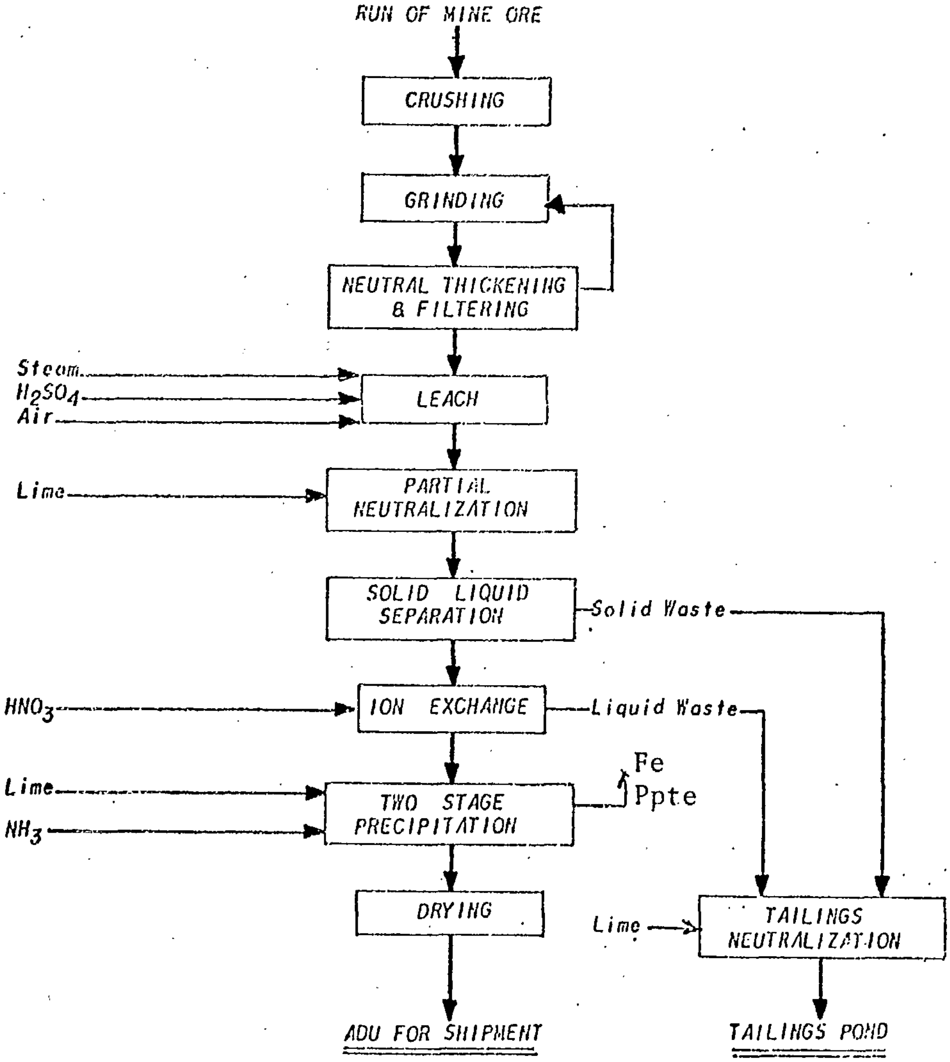

FIGURE 1.2: Acid-Leach Flowsheet (Elliot Lake) (3).

TABLE 1.2

Chemicals Used in Milling Operations

Acid-Leach Process	Amount of Reagent Used (kg per tonne ore milled)
Grinding media	2 - 3
Polyacrylamides	.05
Sulphuric Acid, H_2SO_4	25 - 55
Sodium Chlorate, $NaClO_3$	2.5
Nitric Acid, HNO_3 (60%)	1.6 - 2.5
Ammonia, NH_3	.1 - .5
Lime, CaO	10
Limestone, $CaCO_3$	16
Alkaline-Leach Process	
Sodium Hydroxide, NaOH	5.63
Lime, CaO	5.93
Xanthates	.115
Flocculants	.35
Gums	.0025

Nitric acid has also been suggested as a leaching agent for uranium ores (4, 5). However, because it costs more than sulphuric acid and because of the toxicity of the NO_3^- ion, the use of nitric acid has been little studied.

An interesting development in uranium extraction in Canada is the production of U_3O_8 by in situ leaching (6). This involves the use of bacteria to produce a solution reactive enough to leach uranium from blasted rock underground, and is essentially an acid ferric-ion leach where the bacteria are utilized in the oxidation of the iron to the ferric(+3) state. Annual production of 450, 000 kg U_3O_8 is expected by this method.

1.2.2 The Alkaline-Leach Process

Uranium may also be extracted from the ore by an alkaline-leach process. The high-acid-consuming ore at Beaverlodge is particularly conducive to alkaline leaching. The uranium is dissolved in a sodium carbonate - sodium bicarbonate leach with oxygen as the oxidizing agent after removal of pyrite by flotation. An alkaline-leach flowsheet is shown in Fig 1. 3. and this also shows the flotation and acid-leach circuit which accounts for about 2% of the total ore throughput. The alkaline-leach is highly selective for uranium and consequently no upgrading of the leach-liquor is required; the yellowcake concentrate, sodium diuranate ($Na_2U_2O_7$), is precipitated directly from the clarified solution.

The reagents used in the milling of one tonne of uranium-bearing ore by an alkaline-leach are shown in Table 1. 2.

2. DESCRIPTION OF TAILINGS DISPOSAL OPERATIONS

2.1 The Tailings Disposal Basin

The careful selection of a tailings disposal site is an important prerequisite to good waste management. The tailings area often provides the best opportunity for effluent treatment and control. Ideally, what is required is an impervious basin which can have a controlled outflow point and is located close to the mill. Potential sites for a tailings area may be classified as follows:

(i) Flat ground.

(ii) Side-hill.

(iii) Cross-valley.

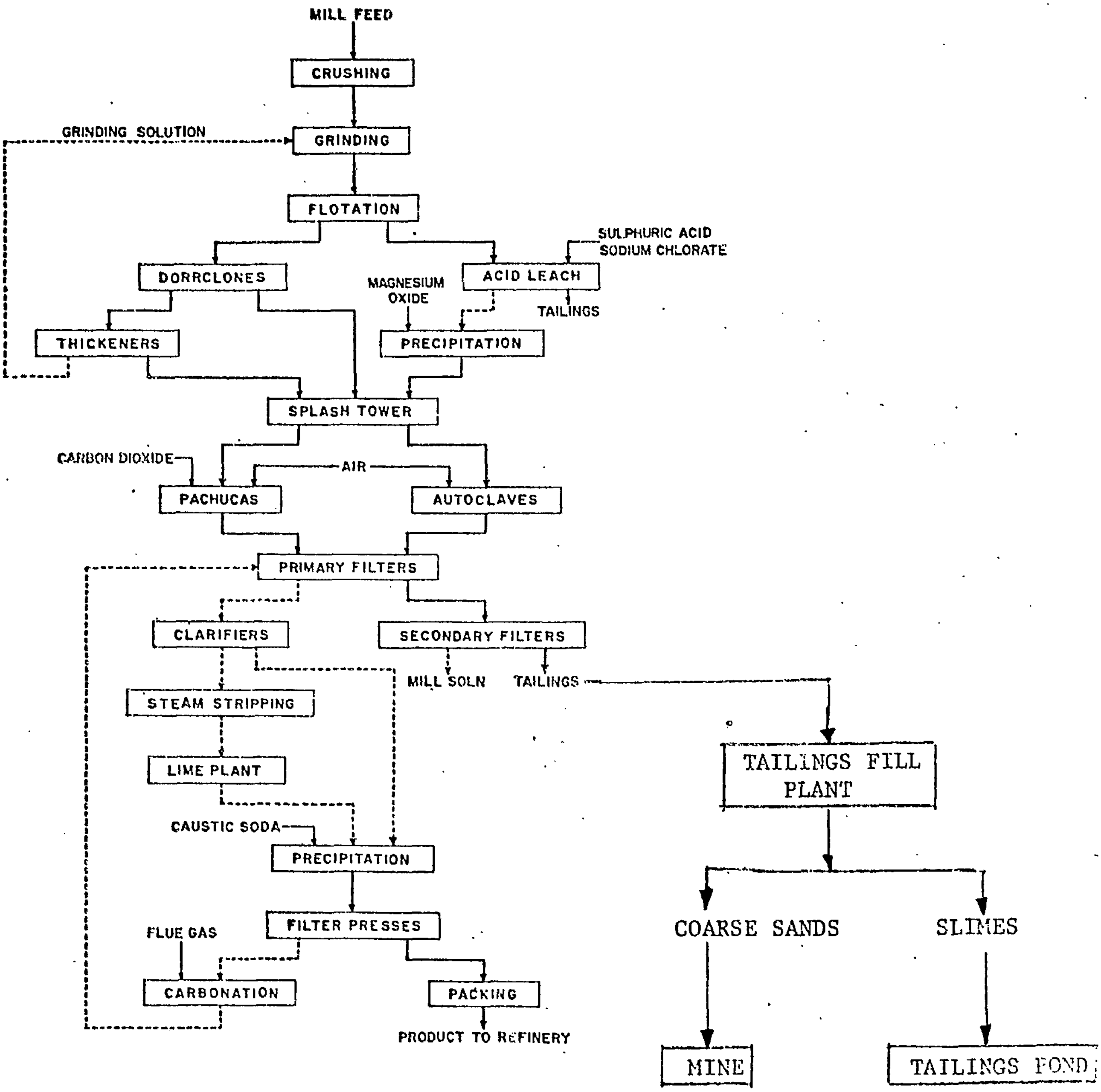

FIGURE 1. 3: Alkaline-Leach Flowsheet (Beaverlodge) (3).

The uranium mining areas of Canada are located in the Canadian Shield and the topography is characterized by numerous lakes, swamps and natural basins which have been utilized for tailings disposal. The result has most often been a cross-valley tailings area, and since the Precambrian rock is impervious, the outflow may be regulated by the construction of suitably located dams. This type of disposal area is preferred since it eliminates the stacking of the tailings behind large high dams and best integrates the tailings area into the surrounding countryside.

All solid waste from the processing plant or mill must be contained in the tailings area. These sites may have areas of 200 hectares* or more and may contain up to 40 million tonnes of tailings. The dams or embankments impounding such large masses of material must be carefully designed and constructed.

2.2. Dam Design and Construction

In the past, dams were often constructed to provide a tailings disposal area which could incorporate the tailings over the life of the mine and little consideration was given to long-term stability. More recently, there has been increasing emphasis on planning for abandonment and a great deal of attention has been focused on the design requirements of tailings dams (7) (8). The major features which require consideration have been identified:

---

* 1 hectare = 2.48 acres.

(i) stability of the dams at both their upstream and downstream faces;

(ii) control of seepage flows through the dam and base of the reservoir;

(iii) ability to stabilize the dams, by vegetation or other means, on abandonment.

Current tailings dams generally meet these requirements: operating companies have built dams with adequate drains; rubber membranes or clay cores have been utilized to minimize seepage, and piezometers have been installed to monitor the phreatic surface. Also, culverts have been carefully constructed and provision has been made for flood conditions. The radioactive nature of uranium tailings makes their permanent containment imperative since a release of radioactive material, through dam failure or overflow, could have consequences long after the physical damage caused has been repaired.

Recently, an alternative approach to the design of a tailings area has been suggested which places less emphasis on the construction of the dams and embankments (9). A thickened tailings discharge, 35 - 60% solids versus the present 25%, is utilized to build a stable conical-shaped tailings area which has lower perimeter dams, smaller settling ponds and results in less seepage than the conventional cross-valley impoundment.

2.3. The Disposal of Tailings

Tailings may be deposited into a tailings area by either point discharge or peripheral discharge. Point discharge can be used only when the decant is located a considerable distance from the discharge point and care must be taken to ensure that there is always adequate retention time for the slimes to settle. The advantage of a peripheral discharge system is that the slimes are continually deposited far from the tailings line which can be located close to the dam. Kealy (8) reports this as the easiest and most practical procedure since some measure of seepage control is automatically provided. Figure 2.1 illustrates the grain-size distribution for a peripheral discharge of tailings. A comparison of the amount of seepage from this system (40% -325 mesh) with a point discharge method revealed the peripheral discharge to be the more desirable.

Current tailings areas in the Elliot Lake region are contained by dams of local gravel or mine waste and use a point discharge. Robinsky's approach to tailings disposal uses a point discharge, but since the slimes are incorporated with the sands, a large settling pond is not required for the thickened discharge (9).

2.4 The Hydrology of a Tailings Area

A lot of attention has been focused on the design and construction of the tailings dams or embankments and their performance with regard to water permeability and transport is well known (7). There has not been much research on the hydrology of the tailings area itself. In the following sections the various sources of water input and modes of water loss are

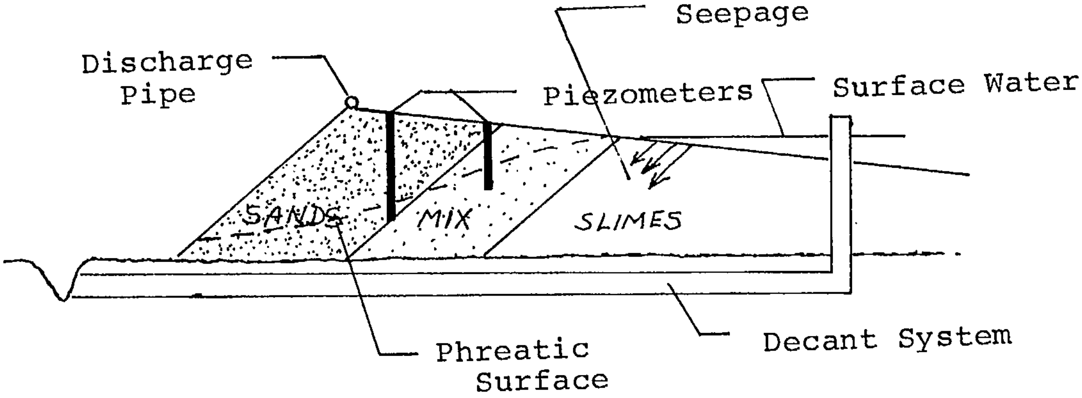

FIGURE 2. 1: Grain Size Distribution for a Peripheral Discharge Operation.

investigated so that a total water balance for a tailings area may be obtained.

The water in a tailings area comes from three distinct, though not necessarily independent, sources, namely:

(i) process water discharged with tailings;

(ii) precipitation, rain and snow;

(iii) surface runoff from surrounding watershed.

These can be represented by a hydrograph like that shown in Figure 2. 2.

Water may be lost from a tailings area by any of the following processes:

(i) evaporation,

(ii) seepage,

(iii) decant or other controlled outflow.

These modes are represented in Fig. 2. 3, and the losses here equal the inflow volume in Fig. 2. 2. It is the outflow of water from a tailings area which provides the problems for the mill operator. A tension exists

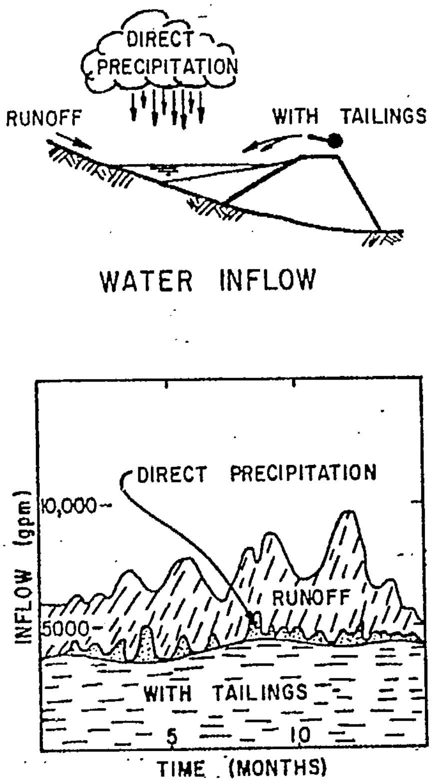

FIGURE 2. 2: Total Inflow Volume (10).

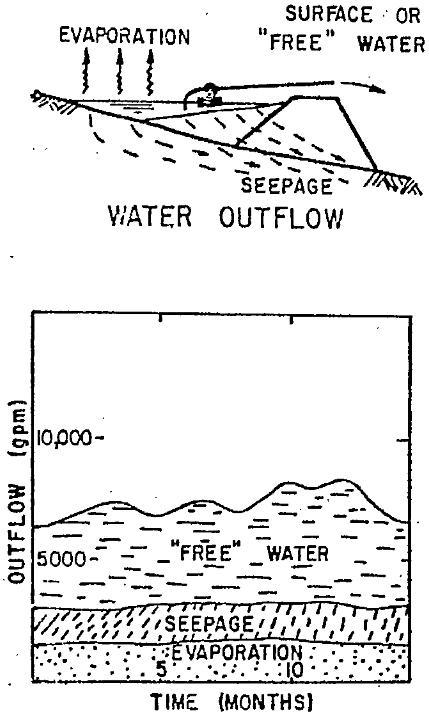

FIGURE 2. 3: Total Outflow Volume (10).

between the most economical means of disposal and the minimization of environmental disturbance. The efficient disposal of tailings and effluents clearly requires the control, and means of manipulation, of the outflow from a tailings area.

2.4.1 Evaporation

The Canadian uranium industry provides a diversity of disposal methods and climatic conditions: northern Saskatchewan is a semi-arid region and Elliot Lake has a wet, temperate climate. Evaporation does provide for some water loss in the summer months but the large volume of water used in the mining and processing operations makes evaporation a minor loss mechanism. The melting of snow accumulated through the winter months further provides a large excess of water in the spring.

2.4.2 Seepage

Seepage is potentially the most troublesome of all water loss mechanisms due to difficulties in detection and control. Water may seep into an aquifer only to emerge much later and pollute streams and lakes, or seepage through a dam may cause its failure. Seepage flows may be low in volume compared to the outflow at the decant, but their high concentration of dissolved salts makes their effects widespread. Furthermore, seepage flows may continue long after mining operations cease. Flows from inactive tailings areas at Elliot Lake have been characterized (2) and a typical example is given in Table 2.1. The rate of flow of this stream was

98.3 m^3 per day resulting in a total daily loading of 524 kg of solids to the environment.

The current practice in treating seepage is to collect as much as possible at a single location and then treat the combined seepage flows by addition of a lime slurry to raise the pH to an acceptable level. Discussion of this practice is found in Chapter 5.

There has been only one comprehensive study of the seepage characteristics of a tailings body as a whole: Kealy et al (11) have shown that the manipulation of the level of ponded water in a tailings area can result in a marked reduction in the volume of seepage.

2.4.3. Process Effluents

The mill-process effluents from both the acid and alkaline leach operations are discharged at an alkaline pH and, when combined with the mine water, result in the pumping into the tailings area of about 1 tonne of water for each tonne of ore milled. Process waste contains the highly soluble reagents added in the mill, (Table 1.2, page 7), and the major contaminants in the final effluents from the Canadian uranium industry are derived from these added chemicals rather than from the ore. The radioisotope radium-226 is the single exception to this. An analysis of typical final-discharge effluents from both types of mills is given in Table 2.2 together with the proposed Federal regulations/guidelines for the uranium industry.

2.5 Inactive Tailings Areas

The spectacular growth and rapid decline of the uranium industry

TABLE 2.1

Example of Seepage Flow from Elliot Lake Area (2)

	ppm
Total solids	6,795
Susp. Solids	265
Diss. Solids	6,530
Total Fe	900
Total Mn	3.9
Total Cu	.9
Total Zn	.7
Chemical Oxygen Demand (COD)	153
Sulphates as $SO_4^=$	4,260
Nitrogen (NH_3)	4.5
Nitrogen (Nitrate)	.02
Nitrogen (Total Kjeldahl)	7.5
Phosphorus as P	2.0

has left a legacy of inactive or abandoned tailings areas which have a multifold detrimental impact on the environment. In the Elliot Lake area there are about 400 hectares of inactive tailings areas. A review of the investigations by those actively involved in the stabilization and rehabilitation of old tailings areas shows the following concerns (2, 12, 13, 14):

TABLE 2.2

Typical Analysis of Final Water Discharge into Watercourses

	Acid-Leach Mill+	Alkaline-Leach Mill+	Federal* Regulations/ Guidelines+
pH	7.0	8.0	6.0
Suspended Solids	5	1	25
Total Dissolved Solids	2250	200	--
Sulphate	1350	75	--
Nitrate	275	.02	--
Ammonia	18	--	--
Calcium	580	17	--
Sodium	10	60	--
Chloride	10	10	--
Iron	0.5	0.06	--
Copper	0.05	0.004	0.3
Lead	0.05	0.005	0.2
Zinc	0.01	0.001	0.5
Nickel	0.03	--	0.5
Cobalt	0.03	--	--
Radium, pCi/ℓ	1-5	3-20	10

+ All ppm except pH and Radium.

* Draft Federal regulations/guidelines for the iron ore, base metal and uranium mining industry.

(i) dusting,

(ii) erosion,

(iii) water pollution from acid seepage,

(iv) heavy metal or radioisotope accumulation in the biosphere,

(v) aesthetics.

Inactive tailings areas dry out quickly as the ponded water drains off and this makes them susceptible to wind erosion. In the spring and fall dehydration of the coarser material occurs through freezing and the wind-blowing of this radioactive material is particularly undesirable. The slimes or finer portion of the tailings retains sufficient moisture and does not become airborne. A study of a uranium tailings basin in Arizona revealed that dust from the tailings resulted in elevated radiation levels outside the controlled area. External radiation levels on the tailings area itself were found to be about 0.7 mR/h which exceeds the recommended continuous whole-body exposure to individuals of the general population (15). A cursory study of the surface of one tailings area in the Elliot Lake area revealed external radiation levels of up to 1.0 mR/h (16). Increased values may be expected from the tailings from higher-grade ore bodies but little can be done to attenuate this radiation, and the present practice is to restrict access to uranium tailings areas.

The problems of inactive or abandoned tailings areas are markedly intensified by the presence of pyrite. Pyrite-containing tailings areas generate acid regardless of the degree of neutralization at the time of disposal. The chemical reactions describing the oxidation and acid production are well known, and may be found elsewhere (17). Since the oxidation of pyrite is thermodynamically favoured, the production of acid is inevitable in the presence of air and water. Furthermore, pyrite oxidation in the tailings takes place considerably faster than is observed in the laboratory because of microbial action (18).

The inactive tailings areas at Elliot Lake present the worst case in terms of acid seepage and its related problems. Most research effort has focused on the rehabilitation of inactive tailings areas by surface stabilization. A vegetated surface will alleviate the offensive nature of the dusting, erosion and aesthetic problems, and it may have a beneficial effect upon the seepage and hydrology by reducing the quantity of oxygen and water penetrating the tailings and consequently limiting the oxidation and acid production. However, a vegetated surface may aggravate the impact of the tailings on the biosphere through heavy metal or radioisotope accumulation in vegetation and wildlife.

2.6 Other Methods of Tailings Disposal.

In addition to the common practice of impoundment of tailings in a cross-valley basin a number of other methods have been suggested or are being practiced by other mining operations. These include disposal in a deep lake (19), use as construction material (20) (21) and underground mine backfilling.

2.6.1 Deep-lake Disposal

Underwater disposal of tailings in a deep lake is attractive for three main reasons:

(i) water is an oxygen transport barrier above the tailings, thereby preventing the acid-generating oxidation reactions of pyrite,

(ii) the need to construct large impervious dams, decant structures and culverts is eliminated,

(iii) there is a clear aesthetic advantage of deep-lake disposal over surface impoundment especially in an area of many lakes.

Hawley (19) has reviewed the problems associated with deep-lake disposal and he concludes it is not a good method when the tailings contain deleterious substances or radioisotopes which may be soluble. One of the uranium producers in Elliot Lake is considering deep-lake disposal as an alternative to further large surface impoundment areas.

2.6.2 Use of Tailings as a Construction Material

Coarse tailings from a U.S. uranium mill were used as fill in a number of construction sites (20). Unfortunately, a radiation problem soon developed in the basements of houses which rapidly forced discontinuation of the practice. Collings et al (21) have investigated the use of Elliot Lake tailings in a number of applications such as building materials or glass, but again the radiation in the tailings mitigates against these uses.

2.6.3. Mine Backfilling

Returning tailings underground has often been suggested as the most obvious and complete means for their disposal. Base metal mines in Canada use this system extensively, and one uranium mine uses about 50%

of the tailings as backfill in a steeply dipping orebody.

The size distribution of unclassified tailings is unsuited to their use as hydraulic backfill and thus a backfill preparation plant is required to produce a suitable material, 90% +200 mesh. A maximum of 60% of the tailings from the Elliot Lake mines could be used underground and the remaining finer portion of the tailings would continue to be discharged above ground. Currently, Elliot Lake mines do not use their tailings as backfill for three major reasons:

(i) a room-and-pillar method of mining is presently employed which does not require the use of backfill. About 15 - 30% of the orebody is tied up in pillars in the Elliot Lake mines. Pillar recovery has not been attempted to date due to the existence of sufficient ore reserves to meet present requirements;

(ii) the gently dipping orebody is unsuited to a cut-and-fill mining method.

(iii) in an investigation on the use of tailings as backfill in an Elliot Lake mine, a high concentration of radon-222 was observed.

Despite these setbacks there is increasing interest in the use of backfill in the Elliot Lake mines to exploit the ore in the pillars, and as a solution to the ever-expanding surface tailings-impoundment basins.

3. THE UNIQUE NATURE OF URANIUM MILL EFFLUENTS

3.1 Introduction

Although the disposal practices of the uranium milling industry are similar to other mining and milling operations in many ways, uranium mining is unique because of its radioactive end-product and waste. This section is concerned with the inherent problems associated with uranium processing because of its radioactivity.

Uranium has fourteen naturally occurring isotopes; the three most abundant and their relative percentages are as follows:

U-238	99.2830%
U-235	0.7110%
U-234	0.0054%

It is clear that the isotope of most concern is U-238, and its decay products are of prime importance. The daughter products of U-238 are shown in Fig. 3.1. The radioactive decay of the U-238 series will tend to equilibrium, and while natural leaching may have removed some isotopes preferentially, the total activity of the ore can be estimated by assuming that an isotope is being formed at the same rate as it decays. The activity of a kilogram of U-238 is 335 microcuries, and since this also will be the activity of each of its thirteen daughters in equilibrium, the quantity of ore containing 1 kg of uranium will have an overall activity of 4.69 millicuries. About 15% of the total radioactivity in the ore entering the mill reportedly leaves in the yellowcake concentrate (22) whereas the remaining 85% is

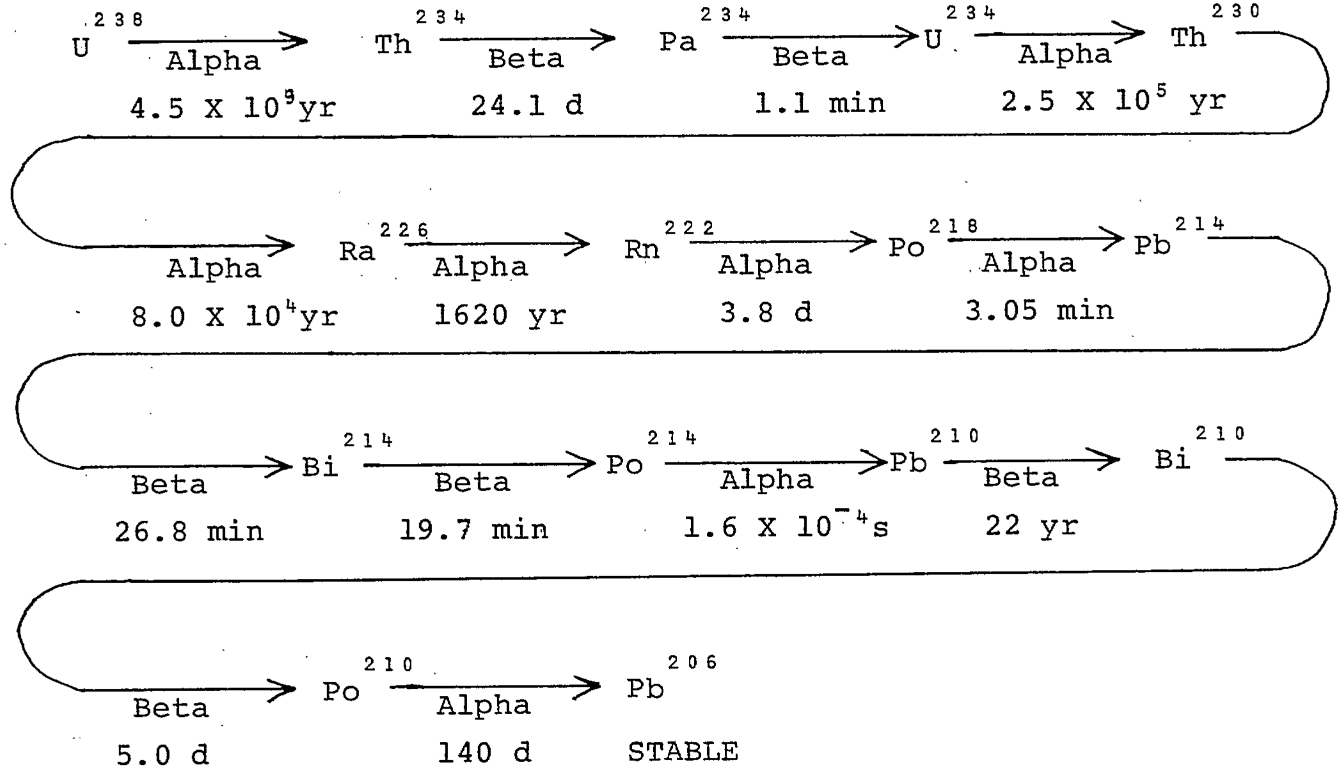

Figure 3.1: The Uranium-238 Series

discharged in the tailings. For a 5000 tonne/day mill processing an ore containing 0.13% U_3O_8, this results in the disposal of about 26 curies per day. If natural thorium is present in the ore then this value will be even higher. It is this large amount of radioactive material which makes the disposal of uranium mill waste unique, and indeed, constitutes a major disposal problem.

3.2 Radioisotopes of Concern

The uranium extraction process is designed for the maximum possible removal of uranium from the ore and, consequently, only small amounts of uranium are left in the tailings. The decay of uranium ensures that there are other hazardous isotopes in the ore, (Fig. 3.1). These isotopes are listed in Table 3.1 in the order of decreasing hazard (23); the maximum permissible concentrations in water, MPC_w, are those recommended by the International Commission on Radiological Protection, ICRP (23). The concentration of all these isotopes is given in terms of the activity of the isotope.

Although the U-238 series is the major contributor to the radioactivity of the ore, two other series, namely U-235 and Th-232, are also of some importance. Uranium-bearing ores always contain U-235 and the other uranium isotopes, but since these isotopes are at least several orders of magnitude less abundant than U-238, they are not considered.

Many uranium-bearing ores contain thorium. In the Agnew Lake area of Ontario, for example, the amount of thorium in the ore

TABLE 3.1

MPC_w Values for Uranium-Radium Series (23)

Isotope	MPCw (pCi/ℓ)	Critical Organ	Half-life	Emission
Ra^{226}	3 (a)	Bone	1620 yr	Alpha
Pb^{210}	33 (b)	Kidney	22 yr	Beta
Po^{210}	233 (b)	Spleen	140 d	Alpha
Th^{230}	600	Bone	8×10^4 yr	Alpha
Th^{234}	6667 (b)	GI tract	24.1 d	Beta
U^{234}	10000 (b)	GI tract	2.5×10^5 yr	Alpha
U^{238}	13300 (b)	GI tract	4.5×10^9 yr	Alpha
Bi^{210}	13300 (b)	GI tract	5 d	Beta
Pa^{234}	(c)	-	1.1 min	Beta
Po^{218}	(c)	-	3.05 min	Alpha
Po^{214}	(c)	-	1.6×10^{-4} s	Alpha
Bi^{214}	(c)	-	19.7 min	Beta
Pb^{214}	(c)	-	26.8 min	Beta
Rn^{222}	(gas)	Lung	3.8 d	Alpha

(a) Standard, Province of Ontario.

(b) 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).

(c) No value given.

exceeds that of uranium and thus the thorium-232 series is significant. This series is shown in Figure 3.2.

The radioactive isotopes of concern from the U-238, U-235 and Th-232 decay series are considered in the following sections.

3.2.1 Radium

Radium-226 has been universally identified as the most hazardous of all isotopes found in uranium mine and mill effluents. Ra-226 has become, for the most part, the "hazard index" for the total radioactivity in process wastes. Ra-226 is the long-lived (half-life 1620 yr) decay product of thorium-230, itself a long-lived daughter of the U-238 series (Fig. 3.1). A low permissible level of Ra-226 has been recommended by all regulatory agencies: the level set in the Province of Ontario for mill effluents is 3 pCi/ℓ (24). One pCi is equivalent to 10^{-12} g of radium-226 and the maximum permissible concentration of radium-226 is therefore, 3×10^{-6} ppm, some five orders of magnitude below that of the toxic heavy metals, for example. At these extremely low concentrations radium often behaves in an anomalous fashion.

Three other isotopes of radium, Ra-223, Ra-224, and Ra-228, also exist in mill effluents. Radium-223 is a decay product of the uranium-235 series, whereas Ra-224 and Ra-228 are products of the decay of the Th-232 series.

The ratio of the activities of Ra-226 to Ra-223 in the ore is constant since the parent elements are present in a fixed ratio and all the isotopes are believed to be in equilibrium. This ratio is determined by the product of the relative abundance and inverse of the half-lives of the uranium parents:

$$\frac{\text{Activity Ra-226}}{\text{Activity Ra-223}} = \frac{99.2830}{0.7110} \times \frac{7.1 \times 10^8}{4.51 \times 10^9} = 22$$

An acid-leach process reportedly dissolves about 1% of the radium from the ore, and since this leaching is a chemical process, it will not differentiate between the various isotopes of radium. Initially, the relative activity of Ra-226 to Ra-223 will thus also be 22 in solution but will not remain constant since the precursors of the radium isotopes, Th-230 and Th-227, have markedly different half-lives, and thorium is over 10 times more soluble in the leaching process than radium. The half-life of Th-227, the precursor of Ra-223, is 18.6 days compared with 8.3 x 10^4 years for Th-230, the precursor of Ra-226. Thus, in the short term, the activity of Ra-223 will increase relative to the activity of Ra-226. Radium-223 grows to a maximum of about 1/6 the activity of Ra-226 within a few weeks, but thereafter rapidly decays. This may not be the case for acid seepage from abandoned tailings areas, however, where a continuous leaching of thorium is occurring. A seepage stream containing thorium will have a source of Ra-233 and thus will result in a higher than expected activity of Ra-223 relative to Ra-226. The activity of Ra-223 may exceed that of Ra-226 since radium is only sparingly leached by an acidic sulphate solution. A typical example of a seepage stream is given in section 3.3.

The other two radium isotopes, Ra-228 and Ra-224, are products of the decay of thorium-232. This series is shown in Fig. 3.2, and is

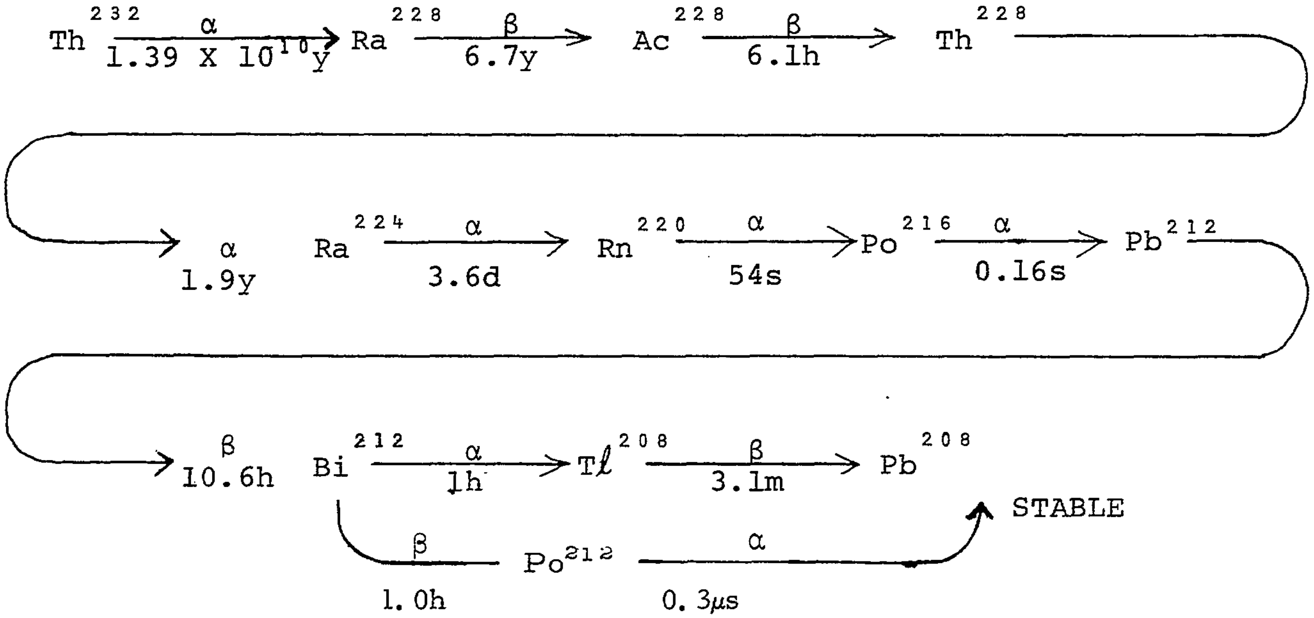

Figure 3.2: Thorium-232 Series.

considered here since it is a component of many Canadian ores.

The activity of Ra-228 in the ore is of course dependent upon the amount of thorium: an ore containing twice as much uranium as thorium has a Ra-228 activity 0.16 times that of Ra-226. When the ratio is increased to twice the amount of thorium to that of uranium, the activity of Ra-228 increases to 0.64 times that of Ra-226. The long half-life of the Th-232 precursor of Ra-228 ensures that the amount of Ra-228 in solution is determined primarily by the solubility of radium, and the ratio of Ra-228 in solution will be approximately that in the ore. The radiological toxicity of Ra-228 is about half that of Ra-226 and although Ra-228 is not on the list of regulated isotopes, it may be a hazard in effluents from mills processing ores containing significant amounts of thorium.

The final radium isotope, Ra-224, is an α-emitter (see Fig. 3.2). The activity of Ra-224 in the ore is the same as that of Ra-228, but the short half-life of Ra-224 (3.6 days) and the relatively long half-life of its precursor, Th-228, means that this isotope decays rapidly and is of little concern in mill effluents or seepage streams.

Radium-226 decays to the radon gas isotope Rn-222. The growth of Rn-222, and the measurement of its activity, is one basis for a Ra-226 analysis. This gives a unique measurement of Ra-226 activity, and overcomes any possible interferences from the other radium isotopes since Rn-222 is the longest lived of the radon gas isotopes produced in the decay of Ra-226, Ra-224 or Ra-223.

Radium-224 and Ra-223 must be measured by α-spectrometry, whereas the β-emitting Ra-228 must be determined by measuring its β activity.

The chemical methods employed in the control of radium in uranium-mill effluents are, of course, not selective for any one radium isotope. Radium-226 is the most toxic and abundant of the four radioisotopes and consequently effluents low in this isotope will also be low in the other isotopes.

3.2.2 Thorium

Thorium has been the object of some interest due to its potential use as a fuel in nuclear reactors. In addition, it has been a saleable by-product from one uranium milling operation from time to time. Ores from the Elliot Lake district contain uranium to thorium ratios of about 2:1 as can be seen from the examples given in Table 3.2. The thorium is present in monazite and brannerite, and, at the acid concentrations employed, the brannerite is the main source of the soluble thorium. Neutralization of the ion exchange barren renders virtually all of the thorium insoluble. However, in the absence of a thorium extraction circuit, this substantial amount of thorium is discharged with the tailings where its ultimate fate is unknown.

Twelve isotopes of thorium are known, having atomic masses from 223 to 234, and all are radioactive. The Th-232 series is shown in Fig. 3.2. The recovery of thorium from the ore causes complications because of the daughter products. Most of the thorium in the ore exists as the naturally occurring radioactive isotope Th-232, whereas most of the activity is due

TABLE 3.2

Uranium-Thorium Grades and Ratios from Selected Elliot Lake Mines (25)

Location	Period	U_3O_8 lb per ton	ThO_2 lb per ton	ThO_2/U_3O_8	Soluble ThO_2 percent
QUIRKE ZONE					
Quirke Mine	composite 1959	2.41	1.00	0.41	--
Quirke Mine	4 months 1960	2.58	0.99	0.38	79
Stanrock Mine	Aug. to Oct. 1958	1.63	0.99	0.61	44
Stanrock Mine	June to Aug. 1959	1.78	0.88	0.50	76
NORDIC ZONE					
Stanleigh Mine	1959 to 1960	2.17	0.35	0.15	--
Milliken Mine	Oct. 1960	2.2	0.39	0.18	61
Nordic Mine	Oct. 1960	2.78	0.50	0.18	68

to Th-230 which has a half-life some 6 orders of magnitude less than the "natural" thorium, Th-232, and hence a much greater specific activity.

Thorium is not recovered in Canada at present.

3.2.3. Lead and Polonium

Little is known about the behaviour of either lead-210 or polonium-218 in the milling process; both isotopes are daughters of radon-222 and their control is important in the underground working environment. One early study found values of Pb-210 up to nine times those of Ra-226 in mill effluents (27), but neutralization is assumed to reduce the level of the soluble Pb-210 sufficiently. For example, concentrations of Pb-210 of from 1 to 8 pCi/ℓ are reported for the final discharge from an Elliot lake tailings area (26). The MPC_w for Pb-210 is 33 pCi/ℓ (23).

3.2.4 Uranium

Existing mills operate with an efficiency of greater than 95% uranium extraction and the uranium remaining in the tailings will further be insoluble except at a low pH. The concentration of uranium in the final effluent from an operating mill is about 50 ppb. Uranium-238 has a MPC_w of 13,300 pCi/ℓ or about 40 ppm. The standard for the uranyl ion in public surface-water supplies in the Province of Ontario is 5 ppm because the chemical toxicity of uranium exceeds its radiological toxicity. The other uranium isotopes are also of little concern because of their removal from the ore and their low specific activity.

3.2.5 Other radioisotopes

The other radioisotopes in Table 3.1 all have extremely short half-lives and so are of little concern in mine or mill effluents. These isotopes require careful control in the underground environment, with standards presently being enforced for radon and radon-daughter levels in air.

3.3 Assessment of the Radiological Hazard of Effluents

The preceding sections have discussed the major radioactive isotopes in uranium mill effluents and their origins: uranium concentrations are minimized because of the economic advantage in their extraction; thorium is rendered insoluble by the routine neutralization of the tailings on discharge; lead and polonium are also apparently removed from solution to an acceptable degree; only radium-226 has a maximum permissible concentration in water which is greatly exceeded in neutralized mill effluents. The radium-226 activity is reduced to 100 to 500 pCi/ℓ on neutralization or about 100 times its allowable concentration.

Previous mention has been made of the use of the radium-226 activity as a radioactive-pollution indicator. It is often assumed that Ra-226 is the sole radioactive isotope in mine or mill effluents which presents a hazard to the environment. However, this assumption may not always be valid. Regulatory bodies favour some sort of mixture rule whereby the cumulative effect of a number of isotopes on the same critical organ in humans is considered.

For a single isotope the following condition must be met:

$$\frac{Ca}{Cm} \leq 1$$

where Ca is the actual concentration of the isotope and Cm the maximum permissible concentration of that same isotope. For a number of isotopes this relationship becomes:

$$\frac{C_1a}{C_1m} + \frac{C_2a}{C_2m} + \frac{C_3a}{C_3m} + \cdots \leq 1$$

Inspection of Table 3.1, and the known toxicity of Th-232 (23), yields the activities of the thorium isotopes in water relative to a radium-226 equivalent as follows:

200 pCi of Th-230 = 1 pCi of Ra-226

200 pCi of Th-232 = 1 pCi of Ra-226.

A sample of acid seepage from an inactive uranium tailings area has the analysis given in Table 3.3.

TABLE 3.3

Seepage from Inactive Uranium Tailings Area

Isotope	Activity, pCi/ℓ
Ra-226	12
Th-230	7,500
Th-232	1,800
Gross α	31,000
Gross β	13,000

This sample exceeds the Ra-226 standard for the Province of Ontario by a factor of 4. Consideration of the cumulative effect of the two thorium isotopes (both thorium and radium are bone-seeking isotopes) results in a total activity of 58.5 pCi/ℓ.

Radioisotope	Actual Activity, pCi/ℓ		Activity expressed as Ra-226 equivalent pCi/ℓ
Ra-226	12		12
Th-230	7500 ÷ 200	=	37.5
Th-232	1800 ÷ 200	=	9
		Total	58.5

This example serves to illustrate the dangers of accepting the Ra-226 activity as the sole hazard indicator.

The concentration of Th-232 equivalent to an activity of 600 pCi/ℓ may be found by the following formula:

$$\text{Concentration } g\ell^{-1} = A C t_{1/2} \times 2.8 \times 10^{-6}$$

where A is the atomic mass of thorium, C is its activity in curies per litre and $t_{1/2}$ its half-life in years. Thus 5.5 ppm Th-232 (or 6.31 ppm ThO_2) is the MPC_w for Th-232.

Repeating this calculation for the other thorium isotope, Th-230, shows 600 pCi/ℓ is equivalent to 32.1×10^{-6} ppm Th-230; the effect of the higher specific activity of Th-230 is evident. A chemical analysis for thorium is clearly a poor assessment of the radiological hazard of thorium in an effluent. However, although uranium is extracted in the milling process, and the uranium precursor of Th-230 is effectively removed, the ratio of the activities of the two isotopes can be found from their mass ratio and their half-lives by taking into consideration the ratio U-238/Th-232 in the ore.

For a uranium:thorium ratio of 2:1, this value is:

$$\text{Activity } \frac{\text{Th-230}}{\text{Th-232}} = \left(\frac{1}{27{,}933}\right)^{*}\left(\text{half-life } \frac{\text{Th-232}}{\text{Th-230}}\right)\left(\frac{\text{At. Wt. Th-232}}{\text{At. Wt. Th-230}}\right) = 6.05$$

Use of this relationship can be made to assess the contribution of the Th-230 isotope to the gross α-activity of an effluent sample; when the chemical concentration of thorium is greater than $\frac{1}{6.05}$ of the MPC_w of Th-232 (5.5 ppm) it is likely that the Th-230 activity exceeds its MPC_w of 600 pCi/ℓ.

Clark (20) suggests that in addition to the analysis for Ra-226 in an effluent, the gross α and gross β activity should be measured. In those instances where the gross α and β exceed those expected for the radium and uranium, analysis for specific thorium isotopes and lead should be performed.

3.4 Methods for the Removal of Radium from Mill Effluents

Tsivoglou and O'Connell (22) have investigated a variety of uranium mills in the United States, and have performed a mass balance on the Ra-226. Mills using both acid and alkaline leaching were examined, and a summary of their results is given in Table 3.4. While other authors report different values for the amount of radium dissolved (5, 27), it is undisputed that the bulk of the radium leaves the mill in the tailings, although it may have been

---

* Assume 1 kg U-238/tonne and 0.5 kg Th-232/tonne ore.
Thus, activity of Th-230 is equal to 335 μCi (the same as its U-238 parent) and its mass is 1.79×10^{-2} g/tonne ore.

$$\text{Thus, mass } \frac{\text{Th-230}}{\text{Th-232}} = \frac{1.79 \times 10^{-2}}{500} = \frac{1}{27{,}933}$$

TABLE 3.4

Dissolved Radium-226 in Uranium Mill Process Flows (22)

Process	Total Radium Dissolved by Leaching %	Dissolved Radium Leaving Mill, %	
		In Tailings Flow	In Yellowcake
Acid Leach	0.4 - 0.7		
Solvent extraction			
Raffinate		80	
Sands and slimes		15	
		95	5
Resin-in-pulp, ion exchange		93	7
Alkaline Leach	1.5 - 2.2		100

dissolved by the leaching solution. It is noteworthy that alkaline leaching dissolves up to 4 times the amount dissolved in the more widely used acid-leach process, and the yellowcake, $Na_2U_2O_7$, contains all of the dissolved radium, so that there is little dissolved radium in mill effluents. This does not mean an alkaline-leach operation will not have any problems due to radioactivity in the effluent since further dissolution of Ra-226 from the tailings will occur. Also the mine water may have concentrations of Ra-226 which require treatment. The acid-leach process dissolves a small amount of the total radium, but virtually all of this is discharged with the tailings (Table 3.4).

3.4.1 Removal of Radium by Precipitation

The most common method for radium removal from effluents involves the use of barium salts, such as barium chloride ($BaCl_2$), which co-precipitate the radium as an insoluble salt, (Ra, Ba)SO_4, according to a reaction of the type:

$$BaCl_2 + Ra^{2+} + SO_4^{2-} \rightleftarrows 2\ Cl^- + (Ra, Ba)SO_4$$

When barium sulphate is precipitated in the presence of radium, the radium atoms are incorporated into the crystal lattice of the barium sulphate or absorbed on the surface of the precipitate. The effective removal of radium is highly dependent upon the precipitation conditions - for example, the anion must be in excess and the concentration of suspended solids must be less than 10 ppm.

A measure of the success of the barium co-precipitation of radium may be gauged from its almost universal use in the control of mine and mill effluents: Canada (26), the United States (28), France (29), Japan (30) and Australia (31) all use some form of barium treatment.

The Canadian practice is to add a barium chloride solution to the clear decant from the tailings pond at a rate of about 10 ppm and allow the precipitated radium-barium sulphate to settle in a lagoon. The resultant final effluent is usually below 3 pCi/ℓ although problems have been encountered in the winter due to short-circuiting of the settling lagoon. Typical results for operating Canadian mills are given in Table 3.5.

All of the treatments with barium salts result in a sludge of (Ra, Ba)SO_4. There is a considerable amount of concern about the long-term stability of this sludge since redissolution of the radium will take

TABLE 3.5

Ra-226 in Effluents in Currently Operating Canadian Uranium Mills (32)

Mine/Mill	$BaCl_2$ added (ppm)	Ra-226 (pCi/ℓ)		Retention Time
		Feed	Overflow	
Eldorado, Beaverlodge	25	25 - 200	3.4 - 7.6	unknown
Rio Algom, Quirke	5 - 15	560 - 1060	1 - 64	48 hr
Denison	4	150 - 550	1 - 5	20 days
Gulf Minerals *	250 - 300	350	1 - 5	-
* design data				

place if the sludge comes into contact with fresh water (33) and this represents a serious limitation of the method.

3.4.2 Removal of radium by ion exchange

In view of the apparent selective absorption of radium on clays (34), ion exchange is perhaps a natural and logical means of radium removal. Arnold and Crouse (34), in a laboratory study, showed that radium could be removed from simulated lime-neutralized acid waste water by absorption onto a number of ion exchange materials. Synthetic and natural zeolites were found to be efficient in radium removal. For example, clinoptilolite could decontaminate about 10,000 bed volumes of a 100 pCi/ℓ radium solution, before the radium concentration in the effluent exceeded 10 pCi/ℓ.

The large volume of water requiring treatment, up to 200 - 300 litres per second, is a major obstacle to the use of ion exchange. Small quantities of water for use as drinking water can be effectively treated.

3.4.3 Other methods of radium removal

Several other methods have been proposed for the removal of radium from mill effluents. These include removal by frothing (35), and precipitation by other reagents along with $BaCl_2$ (29). The use of sodium oleate has been investigated and found to produce a more stable precipitate (29). Experiments at Elliot Lake (36) have shown an increased efficiency of radium removal by the addition of a combination of sodium oleate and barium chloride. Concentrations of oleate in excess of 80 ppm were found to hinder precipitation because of frothing. Typical results are shown in Table 3.6 for a filtered effluent.

TABLE 3.6

Use of Sodium Oleate in Radium Removal (36)

Retention Time	Concentration of Radium, pCi/ℓ		
	Sodium Oleate/$BaCl_2$	$BaCl_2$	Sodium Oleate
48 hr	1	2.4	> 100
24 hr	3.5	3.5	> 100

The use of a cross-linked starch xanthate was investigated as a means of radium removal, but was found to hinder precipitation (36).

3.5 Removal of Thorium

The efficiency of the removal of thorium by neutralization is readily apparent from the data in Table 3.7. The acid-leach mills discharge their final effluent at a pH of at least 7.0. Although up to 80% of the thorium

TABLE 3.7

Effect of pH on Thorium Solubility

pH	Solubility of Thorium, ppm
4.0	110
5.0	31
7.0	0.13

in the ore is dissolved in the acid-leach process, the practice of lime or limestone neutralization produces effluents very low in thorium.

3.6 Future Developments in Effluent Treatment

Uranium mining and milling gives rise to low-level radioactive wastes. Effluents from uranium mills require continuing treatment for radium-226 removal. Radium-226 is the most toxic of all radioisotopes present in effluents. Barium chloride is added to effluents to remove the radium and, generally, the performance of this treatment is satisfactory although radioactive sludges are produced. Similarly, the control of thorium by neutralization produces a finely divided sludge which is disposed of with the tailings. The long-term instability of these sludges has been demonstrated. Future developments in effluent treatment will likely seek to alter or modify the precipitation methods. Two areas of development seem most likely, namely:

(i) production of more stable sludges through modification of the existing treatment technology. An example of this is the use of sodium oleate which reportedly produces a more insoluble precipitate;

(ii) mechanical thickening and separation of the sludges produced. This would closely resemble the developed technology for thickening of the sludges produced in acid mine drainage, for example. The recovery of thorium as an economic by-product would clearly be the best method for its containment.

Much effort has centered on radium-226 because of its toxicity. There are other radioisotopes present in the mill effluents of which little is known; lead-210 and polonium-210 are known to be present. The careful monitoring and control of these two radioisotopes is a likely future development. The concept of assessing the cumulative effect of the radioactivity of an effluent requires detailed knowledge of the behaviour of all the isotopes in that effluent. This will require the development of analytical techniques which can be applied routinely by the mill operators.

Radium-226 appears to be a good "hazard index" for the effluents from operating mills where the pH of the discharge is carefully controlled. Once the pH becomes acid, as is the case for seepage from inactive tailings areas, the activities of a number of other isotopes must be considered if an accurate assessment of the radiological toxocity of the effluent is to be made.

4. NON-RADIOACTIVE LIQUID EFFLUENTS

4.1 Introduction

The radioactive nature of the effluents produced in the processing of uranium ores is unique but,aside from these radioactive aspects, the uranium mine and mill often resemble other mining operations. For example, large quantities of fresh water are required for the mill circuits, and in the milling process this water is contaminated with various mill reagents and substances present in the ore. Before the water can be returned to the environment it must meet provincial and federal government standards for water quality. The increasingly stringent nature of these regulations has meant a continuing research effort for improved effluent control.

The common reagents used in the milling of uranium ores in Canada were listed in a previous chapter, Table 1.2. Many of these reagents are used in numerous other milling operations: for example, lime is used to control acidic effluents. Thus is is reasonable to examine other Canadian operations, and their practices in water treatment and effluent control.

4.2 Current Canadian Practice: Lime Neutralization

The uranium processing industry is by no means unique in its need to practise tailings treatment prior to their discharge to the environment. Furthermore , other Canadian mining and milling operations produce acid flows with high heavy-metal concentrations. Wherever sulphide ores are mined the problem of acid flows is likely. The method generally employed for acid neutralization and heavy-metal removal involves lime addition. The following examples are typical of current Canadian practice, and they illustrate the developments in water-treatment methods.

In the dewatering of the overburden covering the orebody at Falconbridge's Hardy mine, a water-treatment plant was designed to treat highly acidic water which contained large quantities of dissolved iron (37). This project achieved the control of iron and acidity in flows of up to 9000 gpm by the addition of a lime slurry with aeration and agitation and utilized the existing tailings pond as a settling area for the precipitated solids. Mine waste water was employed in making the lime slurry.

Heath Steele Mine in New Brunswick also uses hydrated lime for effluent control (38). Prior to treatment, however, all contaminated water is collected at a common point, along with the effluent from the underground workings. The isolation of uncontaminated drainage and runoff minimizes the amount of water requiring treatment. The contaminated drainage is pumped into a holding pond or to the process-effluent pond. In either case, the acidic effluent is treated with lime to raise the pH and precipitate the heavy metals, zinc and copper in particular. The effluent has a pH of 10.6 and 99.9% of the copper and zinc is removed, illustrating once again the efficient treatment of the low pH and the removal of heavy metals by lime addition.

The uranium mining and milling industry has to treat acidic and heavy-metal bearing effluents from several sources: abandoned tailings continually produce heavily polluted seepage or runoff; the mines are a source of acidic water; and the milling process produces acidic process waste and tailings.

The above examples have illustrated that acid flows can be neutralized and heavy-metal content reduced by lime treatments. The addition of lime is the conventional means of acid and heavy-metal control. The chemical reactions involved in the process may be summarized as follows:

$$CaO + H_2O \rightleftarrows Ca(OH)_2 \qquad \text{(Equation 1)}$$

$$Ca(OH)_2 + H_2SO_4 \rightleftarrows CaSO_4 + 2H_2O \qquad \text{(Equation 2)}$$

$$FeSO_4 + Ca(OH)_2 \rightleftarrows Fe(OH)_2 + CaSO_4 \qquad \text{(Equation 3)}$$

$$Fe(OH)_2 + 1/2H_2O + 1/4O_2 \rightleftarrows Fe(OH)_3 \qquad \text{(Equation 4)}$$

Equation 1 involves the production of OH^- ions which are the effective neutralization and precipitation reagent. Equation 4 illustrates the need for aeration to ensure the oxidation of iron to form the insoluble yellow-boy, $Fe(OH)_3$. In practice this may be hydrated, but it will eventually dehydrate to form Fe_2O_3.

Lime is readily soluble in water, 1.4 g CaO per litre, and this ensures effective pH control. However, as equations 2 and 3 show, lime additions tend to increase the hardness of the water. Furthermore, lime does little to remove sulphate, nitrate or other anions. These effects are readily seen by examination of Table 4.1 which shows the results of lime neutralization of a typical acidic waste (17).

TABLE 4.1

Typical Results for Lime Neutralized Acidic Waste (17)

	Raw Waste ppm	Treated Waste (lime to pH 8.7) ppm	
Total Solids	4180	3880	
Nitrogen (Nitrate)	0.36	3.5	anions
Nitrogen (NH_3)	6.3	4.5	
Total Phosphorus	0.20	0.02	
Sulphates	2280	2140	
Sodium	7	9	highly soluble metals
Potassium	5.1	5.6	
Calcium	101	712	
Iron	960	0.24	
Chromium	0.15	0.00	heavy metals
Cadmium	0.02	0.00	
Zinc	0.97	0.02	
Cobalt	0.47	0.0	
Nickel	0.39	0.0	
Copper	0.96	0.0	
Arsenic	0.38	0.0	
pH	2.61	8.4	acidity
Acidity as $CaCO_3$	1600	14	

Lime neutralization has a major disadvantage in that as a result of precipitation of heavy-metal hydroxides a slowly settling low-density sludge is produced. This low-density thixotropic sludge, containing 1 - 3 wt % solids, can reduce the effective settling area of the lagoon.

Agitation has been employed to facilitate a more rapid settling, but this is difficult in a large lagoon or tailings pond. Currently the sludges produced from uranium mill process wastes are impounded in the tailings pond and thus retention is assured.

4.3 Limestone Neutralization

Limestone can also be used to neutralize acidic waste waters as it reacts in an acidic solution containing sulphate ions as follows:

$$CaCO_3 + H_2SO_4 \rightleftarrows CaSO_4 + CO_2 + H_2O \qquad \text{(Equation 5)}$$

$$CaCO_3 + FeSO_4 + H_2O \rightleftarrows Fe(OH)_2 + CaSO_4 + CO_2 \qquad \text{(Equation 6)}$$

$$Fe(OH)_2 + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightleftarrows Fe(OH)_3 \qquad \text{(Equation 7)}$$

Limestone also produces sludges of heavy metal hydroxides. Nevertheless, the sludges produced in this case have a much greater density than those produced by lime addition(39).

Unfortunately limestone has two major disadvantages (40):

(i) gypsum (calcium sulphate) and iron hydroxide precipitates coat the surface, inhibit further neutralization, and require either elaborate attritional scrubbing or an expensive fine grinding process before the limestone can be used;

(ii) the limestone neutralization proceeds quite slowly as the pH is raised, and its reactivity at pH 6 is approximately 3 orders of magnitude less than at pH 2.

Several investigators have recognized that an effluent treatment process might utilize both lime and limestone neutralization. In particular, Wilmoth (41) found that lime could be employed to polish the water which had been previously treated with limestone and the major advantages of limestone, namely, higher density sludge, cheaper reagent, and greater safety in handling, could be realized.

4.4 Sodium Based Neutralizing Agents

Since both lime, CaO, and limestone, $CaCO_3$, result in the addition of hardness to the water, some attention has focused on the use of other neutralizing agents. The sodium analogues NaOH and Na_2CO_3 have both been investigated in the treatment of acidic waste waters. The chemical reactions involved in both the neutralization and heavy-metal precipitation steps are exactly analogous to those of $Ca(OH)_2$ and $CaCO_3$ except that there will be no addition of Ca^{++} ions, and no resulting hardness. These sodium salts will have no effect upon the removal of sulphate ions, since Na_2SO_4 is very soluble in water.

Sodium-based alkalis are considerably more expensive than lime or limestone, and caustic soda in particular is extremely difficult to handle. The benefit of reduced hardness seems to be offset by these disadvantages (42, 43).

4.5 Ammonia Neutralization

Gaseous ammonia, NH_3, has been considered as a neutralizing agent since it readily produces OH^- ions on dissolution in water:

$$NH_{3(g)} + H_2O \rightleftarrows NH_4^+ + OH^-$$

Ammonia is not recommended as a reagent for the neutralization of acidic waste water because it has a detrimental effect upon water quality and is extremely difficult to handle (43).

4.6 Silicon Alloys

A variety of silicon alloys have been investigated to determine their effectiveness in heavy metal removal (44). The principle involved is similar to the more common cementation reaction whereby copper is deposited on scrap iron. Although the method has applications in the removal of copper, cadmium, lead and mercury, its usefulness in iron removal has not been demonstrated.

4.7 Sulphide Precipitation

Alkaline reagents, such as lime or caustic soda, all remove the heavy-metal contaminants by their precipitation as hydroxides. These hydroxides often have poor settling characteristics and so cause sludge-handling difficulties. It is not surprising, therefore, that some researchers have sought other means for heavy-metal removal. The low solubility of heavy-metal sulphides suggested that this may be a means for metal precipitation. A two-stage process has been developed (45): the water is first treated with lime to a pH of 5.0, then in the second stage barium sulphide is added at pH 6.5 to precipitate the heavy metals not removed as hydroxides. Iron and aluminum are precipitated as hydroxides and settle slowly. Subsequently, the other metals settle rapidly as sulphide precipitates. Typical results obtained for this process are given in Table 4.2.

TABLE 4.2

Results of Two-Stage Process for Heavy Metal Removal (45)

Stage 1	Stage 2	Final Concentration, ppm								
		Fe	Zn	Mn	Cu	Al	Ni	Hg	Cd	As
Lime addition pH 5.0	BaS addition pH 6.5	0	0.2	0.4	0	0	0.13	0	.008	0

This treatment was applied to acid water with an initial pH of 2.6 and a flow rate of 30 gpm. There is evidence of the high toxicity of the sulphide ion (43) which would limit the applicability of this process.

4.8 Use of Tailings in Effluent Treatment

One scheme for the removal of metal ions from mine drainage utilizes the adsorption of metal ions on solid substrates (46). Many oxides and silicate material have an ability to remove metals from solution. The effectiveness of mill tailings in removing contaminants was investigated. Tailings could probably remove heavy metals by three mechanisms:

(i) absorption of metallic cations on silicates,

(ii) precipitation of metal hydroxides due to the natural basicity of the tailings,

(iii) precipitation of metal hydroxides due to the reaction with calcareous components of the tailings.

In a field test, a stationary bed of tailings was found to raise the pH of an acidic stream from 2.85 to 3.5 and to reduce the iron and copper concentration by 14% (46).

This suggests that the diversion of an acidic stream to flow through tailings may well be advantageous. However, in the case of sulphide tailings, this would further aggravate the pollution problem. Also, an acid leaching process, such as that used for uranium extraction, leaves little, if any, residual basicity in the tailings.

4.9 Conclusions

A number of alkaline materials are available for acid neutralization. It appears that since, in general, large volumes of water must be treated, cost and ease of treatment are the most important factors. Lime is the most commonly used alkali. The addition of lime allows the control of the pH of an effluent and thus the removal of heavy metals by precipitation.

In Elliot Lake, the mill effluents are treated with lime and limestone. The decant from active tailings areas has a pH in the range 6.5 - 9.0. However, it is the seepage and runoff from idle and abandoned tailings areas which present a continuing problem. Chemical analysis on the effluent from both active and idle tailings areas is given in Table 4.3. This table shows that the major areas for concern are the idle tailings areas. Currently, this highly polluted water is being treated by lime addition to raise the pH to an acceptable level and remove the metal cations by their precipitation as hydroxides. The radium is reduced by precipitation with barium chloride (see Section 3.4).

Heavy metals and acidity are reduced to acceptable levels by lime neutralization, but anions (such as nitrate and sulphate) and ammonia are to a large degree unaffected.

TABLE 4.3

Chemical Analysis on Effluents from Tailings Areas (47)

	Active Tailings Areas Decant and Seepage	Idle Tailings Areas	
		Seepage	Runoff
*pH	6.5 - 9.0	2.0 - 6.5	3.0 - 4.5
TDS	1000 - 2500	1000 - 6000	300 - 1500
SO_4	600 - 1500	600 - 3200	200 - 1000
NO_3	100 - 200	5 - 10	5 - 10
NH_3	5 - 15	<0.05 - 3	<0.05 - 3
Ca	250 - 450	250 - 600	50 - 350
Fe^{+2}	<0.1	10 - 400	5 - 20
Fe^{+3}	<0.1	10 - 500	5 - 20
Pb	<0.05	<1.0	<0.5
Zn	<0.1	<1.0	<0.5
Cu	<0.1	<1.0	<0.5
Mn	0.01 - 1.0	1 - 3.5	0.5 - 1.5
Ni	<0.1	<1.0	<0.5
Ra_{226} (pCi/ℓ)	10 - 100	10 - 300	<1 - 100
U_3O_8	<1.0	<1.0	<1.0

* All analyses in ppm except pH and Radium-226.

All of the previously discussed treatments result in the need to impound the sludge produced on neutralization in a lagoon or natural settling area. An alternative procedure is possible in the mechanical separation of sludge. Such a procedure is practised in the disposal of municipal wastes, for example. The use of a sludge dewatering process would appear to be too costly, compared to the more readily available use of a natural lake as a settling basin. The long-term problem of disposal or containment of the sludge in these lakes and basins has been given little consideration to date, although some concern has been expressed as to the long-term stability of the sludge produced from uranium milling operations.

4.10 Whither Water Treatment?

In general, the Canadian practice of liquid effluent treatment involves lime addition, and the preceding examples have shown that water quality regulations can be met for both acidity and heavy metals by this practice. Indeed, for the most part, acidity and heavy metals have been the major villains in water pollution. Despite this there is also a need to control total dissolved solids (TDS) and nitrogen compounds. The addition of lime does little to improve a TDS problem; in fact, it may worsen the situation. Similarly, lime additions have little effect upon nitrogen-containing compounds.

4.10.1 The Removal of Nitrogen

Nitrogen-containing compounds exist as ammonium, (NH_4^+), nitrate, (NO_3^-), or in organic compounds such as amines. At high pH values, the ammonium ion is converted to the particularly toxic ammonia molecule, NH_3.

The nitrogen compounds in effluents result from the use of ammonium nitrate as explosive and in the mill circuits. In the milling of uranium, the preferred form of the yellowcake product is the ammonium salt, $(NH_4)_2\,U_2O_7$, and this results in a considerable amount of ammonia in the mill effluent. Furthermore, ammonia is sometimes used as a neutralizing agent in the treatment of acidic mine water. The milling of one tonne of uranium ore can require up to .5 kg of ammonia and 2.5 kg of nitric acid, HNO_3. This is in addition to the explosives used or the losses in solvent extraction circuits. The high solubility of ammonia and nitrate salts ensures their presence in tailings area effluents.

Ammonia may be removed by air stripping or biological denitrification (48). Ion exchange has also been applied to the removal of the ammonium ion (49). Nitrates can be removed by ion exchange (50) or biological denitrification (51).

All of these methods are complex and costly and not particularly suited to the treatment of the large volumes of effluent from current Canadian milling operations.

4.10.2 Sulphate Removal

The sulphate anion, SO_4^{2-}, is often the major contributor to the TDS problem in mill effluents. Sulphate removal can be effected by ion exchange methods. One process in particular utilizes an Amberlite resin in the treatment of an acid mine drainage to produce a potable water (52).

Gilmore (53) has suggested a process which may be applied to effluents from typical Elliot Lake operations. A sulphate concentration of

5800 ppm in an acidic mine drainage water was reduced to <9 ppm by adsorption on the carbonate form of a quaternary ammonium exchanger.

Effluents from the sulphuric acid leaching operations exceed the Ontario government objectives of 500 ppm SO_4^{2-} at present. It is advantageous to have a large excess of sulphate in the effluent, since this promotes efficient radium removal by precipitation as radium-barium sulphate (see Section 3.4).

5. THE MILL PROCESS AS A KEY TO POLLUTION CONTROL

5.1 Introduction

Perhaps because of the large areas of abandoned tailings the study of means of lessening their impact on the environment has mainly concentrated on the nature of the tailings themselves. Indeed, it is clear that careful site selection and disposal practices can go a long way towards a well-managed environment. However, the milling process is the source of many of the pollutants and several of the unit operations in the mill might be modified to produce cleaner effluents and wastes. This section examines the mill circuits with a view to environmental improvement.

5.2 Grinding

The mined ore is crushed underground in a jaw crusher and mine water is used to minimize dust. Before leaching, however, this crushed ore must be ground to a suitable size. (In the case of the Elliot Lake sulphuric acid leach, this is about 45% -200 mesh.) Current practice is generally to wet-grind the ore at pulp densities of 70 - 80% solids in rod and ball mills. The consumption of the steel grinding rods and balls is of the order of 1 - 2 kg per tonne of ore which results in increased iron and sulphate in the leach solution. Media consumption is eliminated in a fully autogenous grinding circuit where the larger pieces of the ore are used as the grinding medium with a resultant decrease in the consumption of leaching reagents. All ores are not amenable to autogenous grinding; there are no fully autogenous mills in Canada at present although Gulf Minerals at Wollaston Lake, Sask. operate a semi-autogenous mill. Grinding processes which use less or no water may also be desirable, e.g., the Arlit uranium mill in Niger which is an example of a low water-consumption autogenour-grinding operation (54).

5.3 Leaching

The most common reagent for the leaching of uranium ore is sulphuric acid (at a pH of less than 0.5). Strong-acid processes have also been investigated (55), and these reportedly necessitate less grinding (to 1 - 2 mm versus the present 45% -200 mesh) and higher pulp densities than those used in acid-leach operations at present, resulting in reduced water use. Sulphuric acid at a concentration of up to 6N is used in these processes. These strong-acid leaching operations take place at 90°C and result in a considerable reduction in acid consumption and hence reduced sulphate contamination. The higher temperatures may necessitate greater power consumption. A nitric acid leach process would also result in less acid consumption since the acid could be recycled.

5.4 Washing Operations

After the leaching of the uranium ore with sulphuric acid, the acidity is adjusted to approximately pH 2 and the pregnant solution is then separated from the solids which are washed by CCD or a filter wash circuit. Barren solutions can be used for the wash, but fresh water is also required. The total water requirements may be as high as 2.5 tonnes per tonne of solids fed to the circuit. Cyclones or rake classifiers may be used to achieve a partial solid-liquid separation and these may reduce the water requirements of the CCD circuit. Nonetheless, it is important that the wash efficiency is maximized to ensure that as little soluble uranium as possible is lost in the tailings.

5.5 Ion Exchange and Solvent Extraction

At present over 80% of Canada's uranium is produced in mills employing both fixed bed and moving bed ion exchange circuits. Lendrum (56) suggests that continuous ion exchange columns may provide an attractive method for upgrading unclarified solutions. Ion exchange operations produce a barren solution in addition to the pregnant uranium solution. This barren solution contains the chemicals used in the loading and eluting steps of the ion exchange column, including nitrate ion, (NO_3^-). Recycling of the barren solution is not possible due to the build-up of nitrate and other impurities.

Solvent extraction is a serious competitor to ion exchange from the viewpoint of environmental protection, and there appears to be a move towards the use of solvent extraction to upgrade the uranium leach liquors in Canada (5). The solvents used in uranium extraction are tertiary amines and alkyl phosphates in a carrier of 90% kerosene. Both of these extractants operate at a pH of 1.5 - 2.0, and so are well suited to an acid leaching process. SX has a major advantage in that the uranium values may be recovered from unfiltered ore leach slurries by a solvent-in-pulp (SIP) method or pulsed column extraction (57).

There are solvent losses in a solvent extraction process, but the technology exists for removal of organics from effluents. Research has been carried out on means of minimization of solvent extraction losses - Lucas and Ritcey (58) categorize solvent losses into four classes:

(i) solubility in the aqueous phase -- approximately 20 ppm,

(ii) entrained solvent with the raffinate discharge,

(iii) adsorbed solvent on slurry particles,

(iv) lost solvent in an aqueous-solid-organic emulsion.

The use of surfactants such as organic sulphonates reduces the entrainment of solvent (58), and flocculants can be utilized to minimize the formation of emulsions. However, at present, it appears that solvent losses must be of the order of 0.1 kg of amine per kg of uranium. This would entail a loss of about 0.5 tonne/day for a 5000 tonne/day mill.

The toxicity of the chemicals used in SX has been investigated and categorized by Hawley (43). The problem is further complicated by the fact that metal ions in solution become more toxic when complexed by organic ligands. Activated charcoal has the capacity to adsorb organic reagents, and thus the technology exists to produce effluents containing less than 1 ppm organics. The used charcoal may be recovered and reactivated by furnace generation. Tests by Ritcey et al (59) for two uranium solvent extraction systems produced the results in Table 5.1 which demonstrate the feasibility of organic removal. This process utilized 10 g carbon per litre treated.

TABLE 5.1

Removal of Organics from SX Process (59)

Solvent System		Characteristics				Solvent Analysis ppm	
Extractant	Modifier	Dilutant	Metal	Anion	pH	Feed	Effluent
Alamine 336	Isodecanol	Shell 140	U	SO_4^{2-}	1.8	6.7	<0.3
DEHPA	TBP	Shell 140	U	SO_4^{2-}	1.8	1.2	0.6

The ease with which acceptable levels of organics in the effluent can be obtained is in sharp contrast to the difficulty of removing ammonia and nitrate. Many of the difficulties encountered with solution upgrading by SX can be minimized by a combination of both IX and SX. The Eluex process utilizes IX as a first upgrading step and a sulphuric acid elution eliminates nitrate ions in the effluent (60). The eluate is then further upgraded by SX.

5.6 Yellowcake Precipitation

In the sulphuric acid leaching operations, the uranium is precipitated from the pregnant solution by addition of ammonia to a pH of about 8. The ammonium diuranate, once dried and packaged, is the finished product of the uranium mills. Previous sections have outlined the difficulty in control and removal of ammonia from mill effluents. It is this precipitation step, requiring up to 0.2 kg NH_3 per kg of U_3O_8, which is a major contributor to the ammonia in effluents. It is reasonable, therefore, to consider other means for precipitating the yellowcake.

There are known alternative methods for the precipitation of yellowcake. Magnesium oxide (MgO) was used originally in Canada and it gives a readily filterable precipitate but has disadvantages in that the addition is difficult to control and the precipitation is slower than with other reagents (61). Furthermore, the yellowcake product is often of a lower grade.

Hydrogen peroxide (H_2O_2) has been investigated as a precipitating reagent and its advantages are given as producing a readily filtered, washed and dried product of greater density (x 1.25 compared to ammonia). The product has a high U_3O_8 content, 90 -95%, and is low in impurities. Table 5.2 gives a comparison of the product purity obtained with different precipitation reagents (62). The costs of using H_2O_2 are reported to be double those of ammonia per kg of U_3O_8 produced. In addition to these increased costs, some producers have contracts for the delivery of ammonium diuranate, further complicating a change from ammonia to hydrogen peroxide precipitation.

The reactivity of hydrogen peroxide, and the danger of fires with organic material, may be a further limitation in its use.

5.7 Water Recycling and Re-use

The current Canadian practice of water recycling and re-use is governed, to a large degree, by the availability of water. This can be readily seen on examination of some British Columbia copper mining operations (63). Figure 5.1 shows the breakdown of tailings water balance

TABLE 5.2

Comparison of the Different Purification Methods (62)

Precipitation Method	Product, %						Solution ppm U_3O_8
	U_3O_8	V_2O_5	Mo	Na	K	Ca	
NH_3	90.3	1.62	0.64	2.04	0.28	0.22	7
$NH_3 + (NH_4)_2SO_4$	89.3	1.61	0.60	0.40	0.06	0.02	7
H_2O_2	96.2	0.46	0.09	0.03	0.006	0.05	2

for a typical mill, and Table 5.3 shows the various water losses and input for several copper milling operations. Inspection of this table shows that recycling and reuse of water R, C and D, occurs in the operations located in dry or moderate climates.

The results in Table 5.3 show that recycling and reuse practice is largely influenced by climate and water availability.

The advantages of maximum water recycling and reuse are summarized by Hawley (17):

(i) significantly reduces the volume of fresh water that is required daily to sustain processing operations,

(ii) significantly reduces the total volume of waste water that is discharged to the environment,

(iii) reduces waste loadings from a property since reagent additions in the mill will, in all probability, be reduced. Also, precipitation, coagulation and settling effects in the tailings area, on a recycle basis, will tend to reduce overall waste loadings,

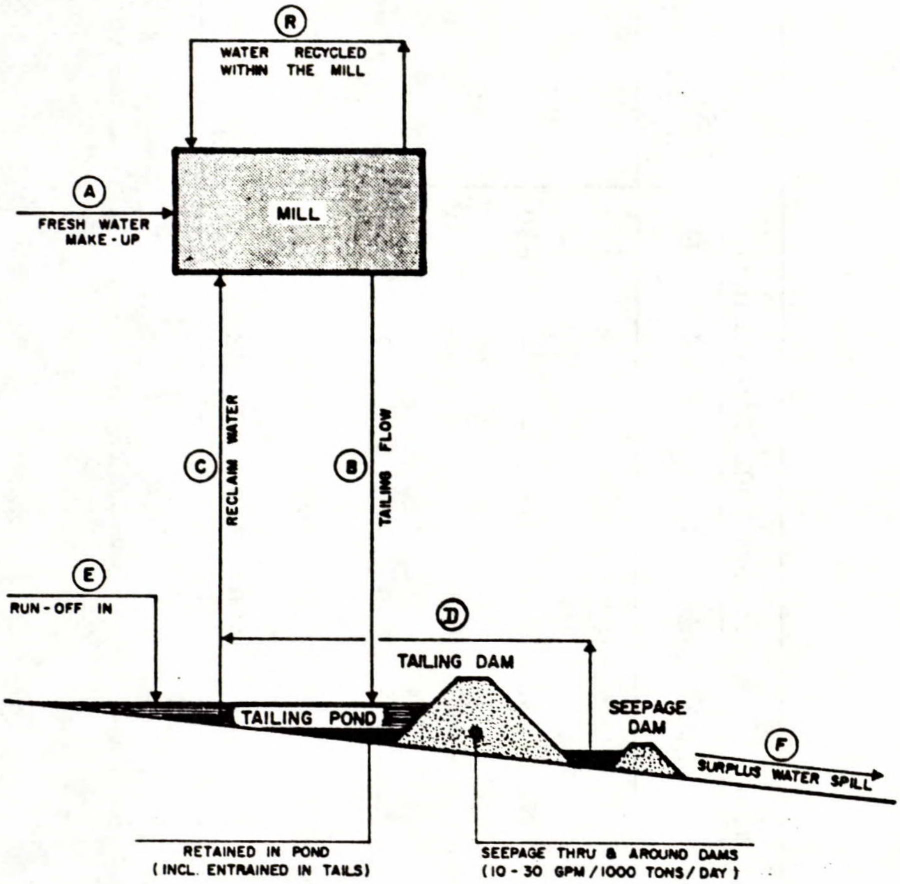

FIGURE 5. 1: Diagram of Tailings Water Balance (63).

(iv) reduces the required size of all waste treatment units due to the smaller volume of all waste flows. Also recycling permits the installation, if necessary, of very efficient and specific waste treatment units that are generally not available in sizes that are able to handle very large volumes of waste flows.

5.7.1 Water recycling - A systems view

Bragg (64) outlines several levels of concern for water recycling and reuse, namely: the "no treatment", "minimum control", and "low-level-system". A flow diagram for the latter is shown in Figure 5.2. This

TABLE 5.3. Tailings Water Balance for some B.C. Mining Operations (63)

Size of Mine T/D milled	Type	Climate	Ppt. in./yr	Water Flow IGM per 1000 T/D milled*							% Reclaimed C/B x 100
				R	A	B	C	D	E	F	
Small 1500	Cu	Wet	100	No	410	410	0	-	-	467	-
Large 3000	Cu	Wet	60	No	630	630	0	-	-	630	-
Small 650	Cu	Moderate	20-30		510	480	0	-	42	440	-
Large 24000	Cu Mo	Moderate	20	Yes	30	490	420	100	33	0	86
Small 1050	Cu Ag Au	Dry	20	Yes	80	360	300	60	-	0	83
Large 25000	Cu Mo	Dry	10-15	Yes	67	400	330	67	42	0	83

* For explanation see Figure 5.1.

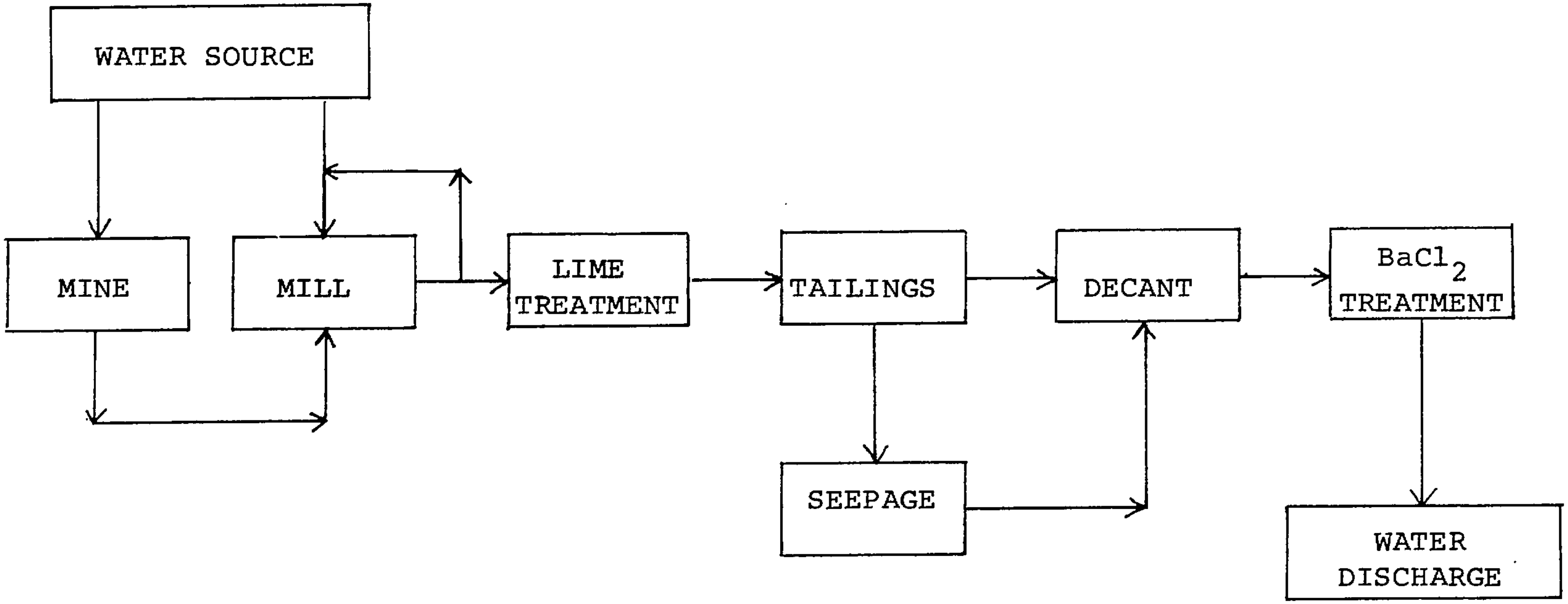

Figure 5.2. Low-Level System for Effluent Control.

corrects some of the difficulties of the "minimum control" level by a recycling of some water within the mill process and entails a unification of mine and mill wastes and a minimum treatment with lime. Dissolved radium is also removed from the tailings-pond decant. The water quality discharged from such a system is discussed in Section 4.1. Lime addition controls the acid and heavy-metal content of the water discharged to the environment to within acceptable limits (see Table 4.3).

Bragg's final level of concern is called the "high-level-systems view" and seeks to correct the shortcomings of the low-level-systems case. In the "high-level-systems view", sludges are separately impounded and treated, and solid wastes are utilized for secondary purposes, as far as possible (64).

Pickett and Joe (65) summarized the water recycling and reuse practice of some Canadian uranium mills as shown in Table 5.4. In the acid-leach mills the water recycling takes place in the grinding and washing circuits. Mine water, which is acidic and contains some dissolved uranium, is used in grinding and in the washing of the solids after leaching. Mine water is not used in the alkaline-leach mill. All unit processing, including grinding and flotation, is done in a concentrated sodium carbonate solution and there is extensive recycling from the thickening and final washing circuits.

A real problem in water recycling involves the buildup of inorganic and organic contaminants. Many operations in mill circuits, e.g., flotation, are sensitive to reagent concentration, which, in the absence of suitable sensors,is impossible to control if recycling is used (66).

TABLE 5.4

Water-Recycling Practice of Some Canadian Mills (65)

Ore, tonnes per day	Leach Process	Water Tonne/Tonne Ore			Recycle Water		
		Fresh	Mine	Recycle	From	To	pH
4200	Acid	0.5 - 1.0	1.0-4.5	-	Thickener	Grinding Counter-Current Decantation	6.9
590	Alkaline	0.27	--	2.3	Thickener Flotation	Mill Circuit	--

A further complication may arise from water temperature, especially in cold winter climates. While mine water is generally at a constant temperature there are large variations in the temperature of the tailings area decant.

Increasingly stringent government regulations suggest water recycling and reuse may become more common. Often the economics of recycling are more attractive than treatment to attain regulatory standards.

6. CONCLUSIONS

1. The uranium industry in Canada is experiencing substantial growth at present, and Elliot Lake continues to be the major producing area. The extraction of the uranium from the ore is achieved mostly by an acid leach, and this appears unlikely to change. One producer is

developing an in situ bacteriological leaching process.

2. Increasing production and lower grade ores will result in the need to dispose of ever-increasing volumes of solid wastes. All indications are that in the immediate future the solid wastes will continue to be impounded in conventional tailings basins. Consequently this will require increasing emphasis and effort in the improved design of dams and tailings areas. It is particularly important to plan for abandonment during the operating life of the mine.

3. Inactive or abandoned tailings areas prove to be a tedious problem which defies ready solutions. The tailings contain pyrite which readily oxidizes to produce an acid drainage problem. These areas have a multi-fold environmental impact through water pollution, dusting, metal and radioisotope toxicities, and their bleak appearance. Stabilization of the surface by vegetation has proved difficult although there has been some limited success. Little is known about the potential beneficial effects that a vegetated tailings surface may have upon water pollution. Revegetation appears to be the only feasible stabilization method at present.

4. Uranium tailings are radioactive, and design of the tailings area for minimal radioactive output is important. The major outputs of radiation from a tailings area are the surface radiation and dissolved radioisotopes in seepage water and runoff.

5. The surface radiation from inactive tailings areas has not been

investigated in any detail, and requires further evaluation. There appears to be no immediate danger of excessive radiation; present levels fall in the range 0.1 - 1.0 mR/hr.

6. The liquid effluents are a major source of radioactive loadings to the environment. This is particularly true for inactive tailings areas where the complexity of the wastes results in effluents containing a number of hazardous radioisotopes.

7. Effluents from active mines appear to contain only radium-226 as a radiological hazard. The current practice of removal and containment of radium by the addition of barium chloride, with an adequate settling area, produces generally acceptable effluents. The tailings are virtually an infinite source of radium and this treatment will likely have to continue in perpetuity. Furthermore, the radium-barium sulphate sludge produced by this treatment must itself ultimately be contained to produce low radioactive output.

8. Although liquid effluents contain a number of radioisotopes (uranium, thorium, radium, lead, polonium), the use of radium-226 as a "hazard indicator" appears satisfactory as long as the pH of the effluent is about neutral. In effluents with a depressed pH (such as seepage from inactive tailings areas) the hazard contribution of other radioisotopes often surpasses that of radium-226.

9. Contamination of surface waters by mill effluents is not restricted to radioisotopes. Uranium mills produce effluents which are high in nitrogen compounds (nitrate and ammonia) and sulphate. The loadings of

these pollutants will markedly increase as the mills expand their production capacities. The large flows of the final discharges make removal of these compounds difficult.

10. Modifications to mill circuits may alleviate many of the non-radioactive effluent problems. The use of solvent extraction or the Eluex process would reduce nitrate loadings, and an alternative to ammonia precipitation of the yellowcake would markedly reduce this pollutant. There appears to be little possibility of reducing sulphate loadings at present. Increased use of water recycling might be used to reduce overall loadings.

7. REFERENCES

1. Anon. Canadian mines handbook 1975-76; Northern Miner Press Ltd., Toronto; 424 p; 1975.

2. Anon. Water pollution from the uranium mining industry in the Elliot Lake and Bancroft areas; v. 2, Ontario Water Resources Commission, Toronto; 106 p; 1972.

3. Anon. Management of waste from the mining and milling of uranium and thorium ores; International Atomic Energy Agency, Ottawa; 8-12 July 1974.

4. Skeaff, J. M. Nitric acid leaching of uranium ore; CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch, Department of Energy, Mines and Resources), Laboratory Report MRP/MSL 75-53 (TR); 20 p; 1975.

5. McCreedy, H. H. Assessment of milling capabilities of uranium plants in Canada; CANMET, Laboratory Report ERP/MSL 75/53(TR); 18 p; 1975.

6. Lang, L. C. & Morrey, W. B. Scientific blasting for in-situ leaching proves successful at Agnew Lake Mines; Eng. Min. J.; v. 177, no. 1, pp 100-102; Jan. 1976.

7. Klohn, E. J. Design and construction of tailings dams; CIM Bulletin; v. 65, no. 720, pp 28-44; April 1972.

8. Kealy, D. Safe design for metal tailings dams ; Mining Cong. J.; pp 51-55, Jan. 1973.

9. Robinsky, E. I. Thickened discharge - a new approach to tailings disposal; CIM Bulletin; v. 68, no. 764, pp 47-53; Dec. 1975.

10. Swaisgood, J. R. & Toland, G. C. Control of water in structures; Tailings disposal today; Ed. C. L. Aplin & G. O. Argall; Miller Freeman Publications, San Francisco; ch. 5, pp 138-163; 1973.

11. Kealy, D. Bush, R. & McDonald, M. Seepage-environmental analysis of the slime zone of a tailings pond; U.S. Bureau of Mines, Report of Investigations 7939; 89p; 1974.

12. Zahary, G. Murray, D. & Hoare, B. Reclamation - a challenge to open-pit mining operations in Canada; Proc. world mining congress, Lima, Peru; Nov. 3-8, 1974.

13. Dunn, R. W. Vegetative stabilization of inactive tailings surfaces. Part 1; Rio Algom Mines Ltd., Elliot Lake; 31p; Dec. 1971.

14. Vivyurka, A. Rehabilitation of uranium mines tailings areas; Can. Min. J.; v. 96; no. 6, pp 44-45; June 1975.

15. Snelling, R. M. & Shearer, S. D. Environmental survey of uranium mill tailings pile, Tuba City, Arizona; Radiological Health Data & Reports; pp 475-487; Nov. 1969.

16. Moffett, D. CANMET, unpublished data.

17. Hawley, J. R. The problem of acid mine drainage in the province of Ontario; Ontario Ministry of the Environment, Toronto; 338 p; 1972.

18. Smith, E. E. & Shumate, K. S. Federal Water Quality Administration, Publication No. 14010 FPS; U.S. Dept of the Interior, Washington, D.C.; 1970.

19. Hawley, J. R. On land or under water? The tailings disposal problem; 77th annual general meeting CIM, Toronto, May 4-8, 1975.

20. Clark, D. A. State-of-the-art: uranium mining, milling and refining industry; U.S. Environmental Protection Agency, EPA-600/2-72-038; 113 p; June 1974.

21. Collings, R. K. Winer, A. A. Feasby, D. G. & Zoldners, N. G. Mineral waste utilization symposium, Chicago, Illinois; May 7-8, 1974.

22. Tsivoglou, E. C. and O'Connell, R. L. Nature, volume and activity of uranium mill wastes; Radiological health and safety in mining and milling of nuclear materials; International Atomic Energy Agency, (IAEA), Vienna; v. 2, pp 123-154; 1964.

23. Anon. Report of committee II on permissible dose for internal radiation; International Commission on Radiological Protection, (ICRP); Part II; Pergamon Press, London; 1959.

24. Anon. Guidelines and criteria for water quality management in Ontario; Ontario Ministry of the Environment, Toronto; June 1973.

25. Robertson, J. A. Geology of township 149 and township 150; Geological Report 57, Ontario Department of Mines, Toronto; 162 p; 1968.

26. Anon. Draft report of radioactivity sub-group to the mining task force for the development of effluent guidelines and regulations for the Canadian mining industry; Environmental Protection Service, Department of the Environment; July 1974.

27. Anon. The control of radium and thorium in the uranium milling industry; Topical report WIN-112; U.S. Atomic Energy Commission, Report AT(49-6)-924; 1960.

28. Beverly, R.C. Unique disposal methods are required for uranium mill wastes; Mining Engineering; v.20, no. 6, pp 52-56; 1968.

29. Chardon, P & Kremer, M. Manutention des dechets solides et liquides du complexe mine-usine des Bois-Noirs de la division du Forez: epuration des effluents; Radiological health and safety in mining and milling of nuclear materials; IAEA, Vienna; v.2, pp 155-178; 1964.

30. Misawa, H. Kanazawa, K. Maruyama, M. Segawa, T. & Ashizawa, T. Solid and liquid wastes at the Ningyo-toge mine; Radiological health and safety in the mining and milling of nuclear materials; IAEA, Vienna; v.2, pp 123-154; 1964.

31. Ryan, R. & Alfredson, P. Laboratory studies of the treatment of liquid waste streams from uranium milling operations; Proc. Australas. Inst. Min. & Metall.; no.253, pp 25-34; March 1975.

32. Smith, H.W. Discussion on control of radium in plant effluents; Mines Branch (CANMET), Extraction Metallurgy Division; Report EMI 74-11; 8 p; Aug. 1974.

33. Shearer, S.D. & Lee, G.F. Leachibility of radium-226 from uranium mill solids and river sediments; Health Phys.; v.10, pp 217-227; 1964.

34. Arnold, W.D. & Crouse, D.J. Radium removal from uranium mill effluents with inorganic ion exchangers; I & EC Process Design & Development; v.4, no. 1, pp 333-337; 1965.

35. Schden, H.M. Rubin, E. & Ghosh, D. Radium removal from uranium mill waste water; J. Water Pollution Control Federation; v.34, pp 1026-1031; 1962.

36. Wellard, J. Rio Algom Ltd., Elliot Lake; Personal Communication.

37. Oka, U.M. & Taylor, W.L. Treatment of acid mine water at Falconbridge's Hardy crown pillar project; CIM Bulletin; v.67, no. 744, pp 43-49; Apr. 1974.

38. Busse, E. Acid drainage control and water treatment at Heath Steele; CIM Bulletin; v.67, no. 750, pp 54-61; Nov. 1974.

39. Ford, C.T. Use of limestone in acid mine drainage treatment; Proc. 5th Symp. Coal Mine Drainage Research; National Coal Association, Washington, D.C.; pp 205-228; 1974.

40. Wentzler, T.M. & Aplan, F.F. Kinetics of limestone dissolution by acid wastewater; 101st AIME Meeting, San Francisco; Feb 20-24, 1972.

41. Wilmoth, R.C. Limestone and limestone-lime neutralization of acid mine drainage; U.S. Environmental Protection Agency, EPA-430/9-73-011; Oct. 1973.

42. Anon. Processes, proceedures and methods to control pollution from mining activities; U.S. Environmental Protection Agency, EPA-4301-73-011; 390 p; Oct. 1973.

43. Hawley, J.R. Use, characteristics and toxicity of mine-mill reagents in Ontario; Ontario Ministry of the Environment, Toronto; 244p; 1972.

44. McKaverly, J.P. Fassinger, W.P. & Stivers, D.A. Removal of heavy metals from water and brine using silicon allows; Environ. Sci. Technol.; v.6, no. 13, pp 1109-1122; 1972.

45. Larson, H.P. Snow, J.K.P. & Ross, L.W. Chemical treatment of metal-bearing mine drainage; J. Water Pollution Control Federation; v.45, no. 8, pp 1682-1695; 1973.

46. Miller, J.D. Removal of dissolved contaminants from mine drainage; U.S. Environmental Protection Agency; EPA-R2-72-130; 53 p; Dec. 1972.

47. Vivyurka, A. Rio Algom Ltd., Elliot Lake; Personal communication.

48. Reeves, T.G. Nitrogen removal: a literative review; J. Water Pollution Control Federation; v.44, no. 10, pp 1895-1908; 1972.

49. Keeple, L.G. Ammonia removal and recovery becomes feasible; Water & Sewage Works; pp 42-43, 62; April 1974.

50. Adams, C. Removing nitrogen from waste water; Envir. Sci. Technol.; v.7, no. 8, pp 696-701; 1973.

51. Anon. Biological denitrification and its application in treatment of high-nitrate waste water; J. Environ. Quality; v.4, no. 2, pp 153-163; 1975.

52. Kunen, R. & Demchalk, J. J. The use of Amberlite® ion exchange resins in treating acid mine waters; Proc. 5th Symp. acid mine drainage research; National Coal Association, Washington, D. C. pp 302-311; 1974.

53. Gilmore, A. J. Sulphate, nitrate and ammonia removal; Proc. Canadian Uranium Producer's Metallurgical Committee (CUPMC) meeting, Ottawa, Ontario, May 15-16, 1975; Ed. H. McCreedy; CANMET, Laboratory Report MRP/MSC 75-152(C); pp 41-57; 1975.

54. Leger, J. E. & Boutonnet, G. Arlit uranium mill uses strong acid leach process; World Mining; pp 40-43; May 1974.

55. Smith, S. E. & Garrett, K. H. Some recent developments in the extraction of uranium from its ores; The Chemical Engineer; v. 268, pp 440-444; Dec. 1972.

56. Lendrum, F. C. Developments in uranium ore processing; CIM Bulletin; v. 67, no. 749, pp 51-53; Sept. 1974.

57. Lewis, B. Solvent-in-pulp studies at Rio Algom; Proc. CUPMC, Ottawa, Ontario, May 15-16, 1975; Ed. H. McCreedy; CANMET, Laboratory Report MRP/MSC 75-152(C); pp 41-57; 1975.

58. Lucas, B. H. & Ritcey, G. M. The use of surfactants to reduce solvent losses in a uranium solvent-in-pulp process; Mines Branch (CANMET), Laboratory Report EMA 74-5; 30 p; March 1974.

59. Ritcey, G. M. Lucas, B. H. & Ashbrook, A. W. Some comments on the loss, recovery and environmental effects of SX reagents used in metallurgical processing; Mines Branch (CANMET), Laboratory Report EMA 73-33; 52 p; Nov. 1973.

60. George, D. R. & Ross, J. R. Improved Eluex process for eluting uranium from ion exchange resins; U. S. Bureau of Mines, Report of Investigations 7227; 10 p; 1972.

61. Ingles, J. C. Manual of analytical methods for the uranium concentrating plant; Mines Branch (CANMET) Monograph 866; 1959.

62. Caropreso, F. E. & Badger, W. P. Hydrogen peroxide precipitation at the Atlas Minerals uranium mill; Trans AIME; v. 254, no. 4, pp 281-284; 1973.

63. Ker, W. A. Water resources of the mining industry in British Columbia; Western Miner; v. 47, no. 12, pp 33-40; Dec. 1974.

64. Bragg, K. Pollution potentials & interactions in mine waste embankments in Canada; Mines Branch (CANMET), Laboratory Report EMA 73-12; 16 p; June 1973.

65. Pickett, D. E. & Joe, E. G. Water recycling experience in Canadian mills; Trans. AIME; v. 256, no. 3, pp 230-235; 1974.

66. Shapp, F. D. & Clifford, K. L. Recycling water in Missouri's new lead belt; Mining Engineering; v. 25, no. 7, pp 68-72; July 1973.

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