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Production of Nuclear Materials and Isotopes

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PREFACE

More than 2,100 papers were submitted by the nations, the specialized agencies, and the International Atomic Energy Agency, which participated in the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. The number of papers was thus about twice that involved in the First Conference. Provision was therefore made to hold five concurrent technical sessions in comparison with the three that were held in 1955. Even so, the percentage of orally presented papers was less in 1958 than in 1955.

In arranging the programme, the Conference Secretariat aimed at achieving a balance, allowing adequate time for presentation of as many papers as possible and, nevertheless, leaving time for discussion of the data presented. Three afternoons were left free of programme activities so that informal meetings and discussions among smaller groups could be arranged. No records of these informal meetings were made.

A scientific editorial team assembled by the United Nations checked and edited all of the material included in these volumes. This team consisted of Mr. John H. Martens, Miss L. Ourom, Dr. Walter M. Barss, Dr. Lewis G. Bassett, Mr. K. R. E. Smith, Martha Gerrard, Mr. F. Hudswell, Betty Guttman, Dr. John H Pomeroy, Mr. W. B. Woollen, Dr. K. S. Singwi, Mr. T. E. F. Carr, Dr. A. C. Kolb, Dr. A. H. S. Matterson, Mr. S. Peter Welgos, Dr. I. D. Rojanski and Dr. David Finkelstein.

The speedy publication of such a vast bulk of literature obviously presents considerable problems. The efforts of the editors have therefore been primarily directed towards scientific accuracy. Editing for style has of necessity been kept to a minimum, and this should be noted particularly in connection with the English translations of certain papers from French, Russian and Spanish.

The Governments of the Union of Soviet Socialist Republics and of Czechoslovakia provided English translations of the papers submitted by them. Similarly, the Government of Canada provided French-language versions of the Canadian papers selected for the French edition. Such assistance from Governments has helped greatly to speed publication.

The task of printing this very large collection of scientific information has been shared by printers in Canada, France, Switzerland, the United Kingdom and the United States of America.

The complete Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy are published in a 33-volume English-language edition as follows:

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Canadian Refining Practice in the Production of Uranium Trioxide by Solvent Extraction with Tributyl Phosphate

By J. C. Burger and J. McN. Jardine *

The discovery of pitchblende on the shores of Great Bear Lake was made by Gilbert A. LaBine in 1930.[1] A refinery, mainly for the recovery of radium, was built at Port Hope, Ontario, in 1932. Seven tons of chemicals and other materials were required to one ton of concentrates, and the Port Hope site was chosen because it was located in Southern Ontario close to the source of supply of basic chemicals. Since there is about one ton of uranium in equilibrium with one gram of radium, uranium was a rather embarrassing by-product in the early days of radium refining. At that time the chief use of uranium was in the ceramic industry, where it was used as a colour for pottery and chinaware.

With the discovery of nuclear fission in 1938, the possibility of the production of vast quantities of energy from uranium became apparent. The mine at Great Bear Lake, which had been closed from June 1940 to May 1942, was reopened. In 1943, Eldorado Mining and Refining Company began production at Port Hope of tonnage quantities of U_3O_8 of approximately 96% purity from Great Bear Lake and Belgian Congo concentrates. The U_3O_8 was shipped to the United States for further refining.

In 1947, Eldorado produced a small quantity of purified uranyl nitrate by fractional crystallization. This was further purified by precipitation as uranium tetroxide and was then used for the production of uranium metal by reduction with calcium in a pilot plant of the Dominion Magnesium Company at Haley, Ontario. In March 1948, about 90 kg (200 lb) of purified uranyl nitrate was produced on a laboratory scale by continuous ether extraction.

In 1949, a smelting process[2] was developed at Port Hope to separate uranium from other valuable constituents of radium gravity concentrate (cobalt, nickel, copper, silver and bismuth).

In this process 99.9% of the uranium as UO_2 went into the slag while the other valuable elements appeared in the speiss. The speiss was sold to a cobalt refinery for the recovery of cobalt, nickel, copper and silver. The molten slag was granulated by passing it into a stream of water. It was ground in a ball mill, digested with nitric acid, and uranium was recovered from the filtered liquors by ether or hexone extraction.

A pilot plant, based on the ether-extraction plant of the United Kingdom Atomic Energy Authority at Springfields, Lancs., was set up to carry out extraction work on slags. Although the pilot plant was designed for ether extraction, ether was never used as an extractant. In laboratory tests, hexone (methyl-isobutylketone) had been found to be a better extractant and was therefore used; tests had shown a recovery of 99.7% of the U_3O_8 in two equal-volume extractions. The pilot plant operated through 1950 to May 1951, yielding a product only slightly less pure than that made by ether extraction.

In mid-1951, tributyl phosphate was first tested at Eldorado as an extractant for uranium. An intensive programme was undertaken on slurry extraction using tributyl phosphate (TBP) in a kerosene diluent. Kerosene is a saturated hydrocarbon with a flash point of about 60°C (140°F). The Catalytic Construction Company of Philadelphia was engaged to design a complete solvent-extraction process for the refining of uranium for Eldorado.

The initial plant designed by the Catalytic Construction Company was based on the smelting of the Great Bear Lake gravity concentrates, then digesting and extracting the pulverized slag mixed with uranium-bearing chemical concentrates from other sources. Because of the large capital costs of the proposed refinery, and the limited known reserves of uranium in Canada at that time (1952), further action was deferred. A modified flow-sheet was then designed which did not include the smelting process. This modification involved the direct digestion of a mixture of Great Bear Lake gravity concentrates with other chemical precipitates, followed by slurry extraction. The over-all cost estimates seemed far more favourable, and a decision was made to proceed with further development on the modified process.

As a result it was found that direct digestion of feed materials followed by solvent extraction of the slurry could be carried out with recovery and purity of the product better than any previously obtained. These results were confirmed in pilot-plant operations

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* Refining Division, Eldorado Mining and Refining Ltd., Port Hope, Ontario.

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Table 1. Chemical Analysis of Typical Feed Materials Received at the Port Hope Refinery

Per cent (as received)

Feed	*A*	*B*	*C*	*D*	*E*	*F*	*G*
U_3O_8	14.0	40.0	74.0	72.0	55.0	80.0	62.0
Ca	4.2	0.5	0.5	0.5	0.8	1.5	0.2
CO_3^{--}			2.0				
Cl	0.06	0.10	0.02	0.12	0.12	0.05	0.03
F	0.15	0.04	0.01	0.02	0.04	0.06	0.2
P_2O_5	2.0	10.0	0.2	0.4	0.3	0.2	0.2
SO_4^{--}	20.0[a]		1.0	1.0	1.0	2.0	0.5
Th	0.02	0.02	0.02	0.02	1.0	0.7	0.8
V_2O_5	0.3	0.3	1.2	0.03	0.1	0.01	< 0.01
HCl insol.	25.0	4.5	1.5	2.5	4.0	0.7	5.0
Loss at 110°C (24 hr)	0.2	6.0	4.0	6.0	8.0	1.5	2.5

[a] Occurs as sulfide in the concentrate.

at Port Hope in June and July of 1953, and at the National Lead Company of Ohio in February and March of 1954. The tests proved conclusively that a metal-grade oxide could be produced, and construction of a solvent-extraction plant was approved. This plant was constructed within the walls of the old extraction plant.

The new solvent-extraction plant began to operate in June 1955. The plant and its operations are described as follows: (1) dry feeds handling and digestion, (2) solvent extraction and solvent treatment, (3) boildown and denitration, (4) raffinate evaporation and treatment, (5) nitric acid recovery and (6) sump recovery.

DRY FEEDS HANDLING AND DIGESTION

With the exception of the Great Bear Lake gravity concentrates, the feed materials received at the Port Hope refinery are chemical precipitates containing between 40% and 80% U_3O_8. Analyses of typical feed materials are given in Tables 1 and 2.

The Great Bear Lake gravity concentrates (14% U_3O_8) are currently being received in 45-kg (100-lb) bags, but future shipments will be made in 100-litre (25-Imp. gal) drums similar to those used for other feeds. They are weighed, sampled, and the ore is crushed and ground to a particle size less than 0.177 mm (-80 mesh) in a rod mill. The concentrate is then stored in 100-litre (25-gal) drums until required. A typical analysis of the Great Bear Lake gravity concentrates is listed under "*A*" in Tables 1 and 2.

Other feed materials are received in 100-litre (25-gal) drums containing from 180 to 270 kg (400 to 600 lb) of material. After sampling, the drums are loaded onto wooden pallets, and are taken to the storage area by fork-lift truck.

Table 2. Spectrographic Analysis of Typical Feed Materials Received at the Port Hope Refinery

Per cent (as received)

Feed	*A*	*B*	*C*	*D*	*E*	*F*	*G*
Ag	0.04	0.01	—	—	—	—	—
Al	4.0	10.0	0.2	0.1	0.6	0.1	0.2
As	14.0	10.0	0.04	0.02	0.08	—	—
B	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Bi	0.9	1.0	—	—	—	—	—
Ca	4.2	0.5	0.5	0.5	0.8	1.5	0.2
Cd	—	—	—	—	—	—	—
Co	3.3	0.03	—	—	—	—	—
Cr	0.01	—	—	—	—	—	—
Cu	4.8	7.6	0.02	0.01	0.01	0.01	0.02
Fe	12.0	0.6	0.4	1.0	8.0	0.3	2.0
Mg	4.9	0.5	0.2	12.0	14.0	1.0	15.0
Mn	0.6	0.2	0.01	0.01	0.1	< 0.01	0.02
Mo	0.04	0.01	< 0.01	0.01	0.01	0.01	0.01
Na	—	—	12.0	1.0	2.7	5.0	1.0
Ni	2.9	—	—	—	—	—	—
Pb	1.5	1.0	0.04	< 0.01	—	—	—
Sb	0.1	0.1	—	—	—	—	—
Si	12.0	1.4	1.0	1.1	2.1	1.0	1.0
Ti		0.2	0.1	0.02	< 0.01	0.1	
Y	0.14	0.003	0.02	0.0005	0.04	0.02	0.04
Lanthanides							
Dy	0.04	0.001	0.008	0.0002	0.002	0.002	0.006
Gd	0.04	0.001	0.004	0.0001	0.002	0.001	0.006

The feed materials are conveyed by lift truck to the blending area. A photograph of this area is shown in Fig. 1. The percentage of each feed can be varied within fairly wide limits, but is designed to give a slurry with a uranium content of approximately 300 g U/litre. A typical blend is as follows (the letters correspond to those given in Tables 1 and 2):

Feed	*Amount wt %*	*U_3O_8 wt %*
A	15	13.3
B	10	40.0
C	25	71.7
D	25	74.2
E	5	52.3
F	20	81.5
Total	100	61.5 (weighted av)

The drums are emptied in the proper proportions into the boot of a bucket elevator. The boot is equipped with a grate and a magnetic separator to remove tramp materials. The feed is carried by bucket-elevator to a screw-conveyor which in turn feeds one of three Sprout-Walden ribbon-type blenders. Each batch is blended for approximately one hour. The mixed feed is discharged through another screw-conveyor to a bucket-elevator and this passes the feed to the top floor of the building which houses the digestion tanks.

The feed is discharged into a surge-hopper located above the first of three digestion tanks. A constant flow of feed is maintained by an Omega gravimetric feeder, which discharges through a seal leg to the first digestion vessel. Nitric acid (about 55 wt %) which has been recovered from another part of the process is continuously fed at a controlled rate to the first digestor. The slurry cascades into the second digestion tank and then to the third one. This is a large tank and is the feed tank for the slurry-extraction process. The first two tanks are provided with cooling water and steam lines to control the temperature of the reaction. The third tank is equipped with cooling coils to lower the temperature of the slurry to 35°C (95°F) before extraction. The slurry contains about 300 g U/l, is 3*N* in free nitric acid, and has a density of 1.6 g/ml. Control of both the uranium content and the free acid in the slurry is maintained by periodic sampling, and the flow rates of feed materials and nitric acid can be adjusted.

The hot acidic gases produced in digestion are drawn off in a vent system and are contacted by a circulating water stream in the fume scrubber. Nitric acid is condensed, and a considerable proportion of the nitrogen-oxide gases is converted into nitric acid in the fume scrubber. The aqueous stream used for scrubbing the gases is scrub liquor recycled from the scrub column in the extraction area. This liquor overflows into the first digestion vessel and is used to maintain the slurry at proper density. Water can be added if required. The nitrogen-oxide gases which are vented from the scrubber are converted to nitric acid.

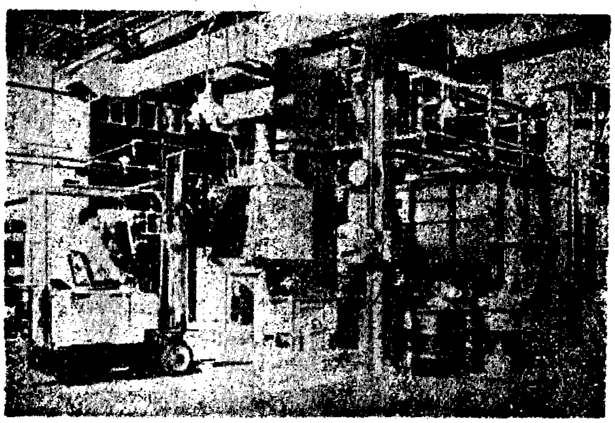

Figure 1. Blending area. A drum of chemical precipitate about to be discharged into boot of bucket conveyor. Sprout-Walden ribbon-type blenders in background

SOLVENT EXTRACTION AND SOLVENT TREATMENT

The solvent-extraction and solvent-treatment area has three important tasks to perform: (1) to recover more than 99% of the uranium from the slurry, (2) to produce a pure uranyl nitrate solution, and (3) to recover and treat solvent for further use. The extraction of uranium from the slurry and the production of a very pure uranium solution is accomplished in three pulse-columns.

The digest-liquor feed passing to the extraction column contains uranyl nitrate, other metal nitrates, free nitric acid, certain insoluble material, and water. There are also small amounts of sulfate, phosphate and arsenates. The uranyl nitrate is selectively extracted from this solution into the organic phase (25 vol % TBP in kerosene) according to the following reaction.

$$UO_2{}^{++}{}_{(Aq)} + 2NO_3{}^{-}{}_{(Aq)} + 2TBP_{(Org)} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP_{(Org)}.$$

The kerosene is used as an inert diluent for the tributyl phosphate. It lowers the density and viscosity of the organic phase, thereby aiding the mass transfer of the uranyl nitrate.

The salting-out effect of the nitrate ion favours the transfer of uranium into the organic phase, and it is for this reason that a high concentration of nitric acid (3*N*) is employed in the extraction column. The absence of the salting-out agent in the re-extraction column facilitates the transfer of uranium to the aqueous phase (de-ionized water).

The main pieces of equipment in the solvent-extraction section are three pulse-columns—the extraction column, the scrub column, and the re-extraction column. Two main streams, an aqueous one and a solvent one, enter each column with the aqueous stream entering at the top and the solvent stream at the bottom. This is, of course, counter-current extraction, since the liquids are flowing in opposite directions, one through the other.

Table 3

Column	Pulse pump amplitude, cm	in.	Frequency, cycles/min	Effective column height, m	ft	Diameter of holes, mm	in.	Theoretical stages
Extraction	2.7	1.1	55	11.5	37.5	4.8	0.187	6
Scrub	1.8	0.7	25	11.5	37.5	3.2	0.125	4
Re-extraction	1.3	0.5	40	7.5	25.0	3.2	0.125	6

Each of the columns provides intimate contacting by pulsing the counter-current flow of the two phases. Pulses are provided by pulse pumps with Teflon bellows. The pumps, one of which is shown in Fig. 2, are located on upper floors of the extraction area about 4.5 m (15 ft) below the top liquid level in the column. The pumps are located here in order to reduce back pressure on them.

Each of the columns is packed with a series of stainless-steel trays which have holes in them. The holes represent 23% of the area and are spaced 5 cm (2 in.) apart.

Design data on the columns are given in Table 3. The actual height of each column including disengaging sections is 4 m (12 ft) greater than the effective heights given in Table 3.

Operating flow rates in the solvent-extraction area are:

Column	Flow rates, litres/min Org.	Aq.	Ratio Org./Aq.
Extraction	100	25.0	4
Scrub	100	5.9	17
Re-extraction	100	66.8	1.5
Solvent treatment	100	4.1	25

Slurry at 300 g U/l, 3*N* in free nitric acid, is pumped from the column feed-tank to a small plastic tank situated above the extraction column. From here it is fed continuously by an Omega Roto-dip feeder into the column below the disengaging section. The speed of rotation of this feeder is controlled either automatically or manually, and is set to give an extract density 0.005 g/ml below the density obtained if the solution was saturated with slurry containing 300 g U/l, 3*N* in HNO_3. At present the saturation density is 0.972 g/ml at 35°C (95°F) with a solvent of 25% TBP in kerosene.

Solvent in equilibrium with 3*N* nitric acid (density 0.845 g/ml at 35°C (95°F)) is pumped into the bottom of the extraction column, and it flows countercurrent to the aqueous stream. The density of the solvent at the top of the column is kept as close to the saturation density as possible in order to minimize the extraction of thorium and other impurities. The organic phase is passed into a settling tank, through a DeLaval hermetic-type centrifuge to remove solids and any entrained aqueous phase, and thence to the bottom of the scrub column.

In the scrub column, the organic-uranyl nitrate solution is contacted with a small quantity of de-ionized water to remove impurities and nitric acid. The scrub liquor containing 220 g U/l and 2*N* in free nitric acid is passed to the fume-scrubbing tank in the digestion area, and from there it returns to the first digestion tank.

The purified extract is then fed to the re-extraction column, and brought into contact with a large quantity of de-ionized water. This operation transfers the uranium back to the aqueous phase. The aqueous product containing uranyl nitrate is cooled, and after entrained TBP has been removed from it by a skimmer, it is concentrated and denitrated. The step where the volume is reduced by boiling is known as " boildown ".

The solvent from the re-extraction column flows into a tank where it is mixed with a 7 wt % sodium carbonate solution. The mixture is then passed to two DeLaval industrial centrifuges arranged in parallel; these separate the organic and aqueous phases. The sodium carbonate removes hydrolysis products formed from TBP, and most of the residual uranium is left in the solvent. The solvent is sent to storage, and the sodium-carbonate solution is sent to the sump-treatment area.

BOILDOWN AND DENITRATION

The area for boildown and denitration contains equipment in which the purified solution containing uranyl nitrate is converted to granular uranium trioxide. This conversion is performed in two steps. The first step consists of a concentration operation where the aqueous solution is boiled down to molten uranyl nitrate hexahydrate (UNH). The second step consists of a thermal decomposition of this hydrate to the granular uranium trioxide.

The uranyl-nitrate liquor from the re-extraction column is passed into a surge tank, and from there through two stainless-steel micro-metallic filters in

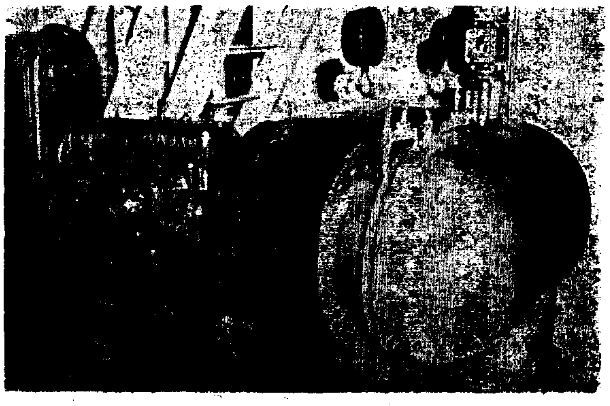

Figure 2. A pulse pump

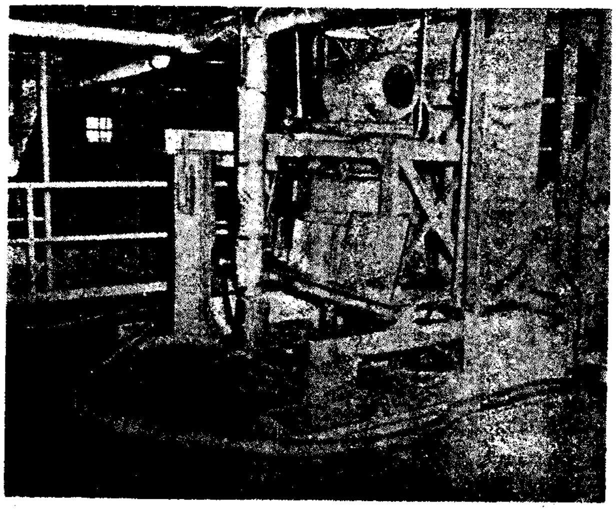

Figure 3. Denitration reactor. The top of the reactor is at floor level. A section of the stainless steel gulping tube is shown on the floor

series (10-micron pore size) into the first of two thermosyphon evaporators. In the first evaporator it is concentrated to 47 wt % uranyl nitrate. Solvent is stripped from the uranyl nitrate in a column packed with Raschig rings located above the flash chamber of the first evaporator; steam evolved from the flash chamber is used for stripping. The steam produced during the flashing passes through an entrainment separator before it is discharged to the atmosphere.

The first evaporator is larger than the second and was designed to be capable of converting the UNH into a 78 wt % concentrate of UN. This is not normally done, however, because the larger surface area contributes to increased corrosion, resulting in an iron content in the UO_3 product over the specified value of 30 ppm.

The level of the liquid in the first evaporator is maintained constant by continuously transferring a portion from its lowest region (bottoms) to the second evaporator. The recirculation pump in the second evaporator removes the bottoms from the first unit and passes the 47 wt % UN together with bottoms from the second evaporator through a heat exchanger. The superheated liquid is flashed after it leaves the heat exchanger to produce 78.5 wt % UN.

A portion of the 78.5 wt % UN bottoms maintained in the second-evaporator flash drum is removed periodically to any one of three reactors for denitration. These reactors (Fig. 3) are electrically heated, and operate approximately on a seven-hour batchwise denitration cycle.

The cycle is as follows:

Period	*Reaction*
1st hour	H_2O evolved
2nd hour	H_2O, NO_2, O_2 evolved
3rd to 5th hours	NO_2, O_2 evolved
6th to 7th hours	Product gulped—recharged

The UO_3 product, which is usually in granular powder form, is manually gulped from the unit by a vacuum system, and cooled from approximately 210°C to 66°C (400° to 150°F) in a jacketed section of the exhaust piping. This is done to prevent deterioration of the bags in the dust collector in which the finely divided dust is collected. The large particles from the cyclone separator and the finely divided dust from the dust collector are discharged to a Mikropulverizer. The UO_3 product is carried by vibrating conveyor to a hopper in the packaging area. The product is continuously sampled as it passes from this hopper into 100-litre (25-gal) drums, the size currently used for shipping the purified product. (See Fig. 4.)

RAFFINATE EVAPORATION AND TREATMENT

The raffinate-treatment section of the plant has two main functions: (i) recovery of nitric acid from the raffinate and (ii) chemical treatment of the raffinate so that it can be safely discarded.

The nitric acid is recovered by the addition of sulfuric acid to the raffinate followed by evaporation in a forced-circulation horizontal-tube evaporator. Treatment of the raffinate for disposal is by neutralization with a slurry of dolomitic hydrate.

The aqueous raffinate from the extraction column, which consistently runs less than 0.1 g U/l, is pumped from the extraction area into one or three raffinate hold-tanks. These tanks are operated in parallel.

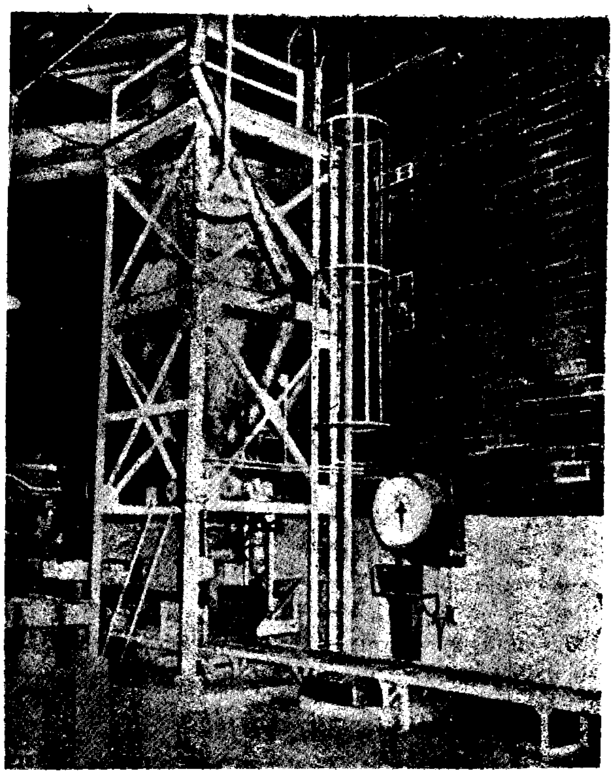

Figure 4. Packaging hopper. The uranium trioxide is fed to this stainless-steel hopper by vibrating conveyor, then put into drums for shipment

Table 4

Source	Temp, °C	Temp, °F	Composition, wt %, wet basis NO_2	NO	O_2	N_2	H_2O
Denitration	40.5	105	3.5	13.8	25.6	54.3	2.8
Digestion	65.5	150	34.1	48.9	2.2	9.1	5.7

While one is being filled, another is being discharged, and the third being analysed. Raffinate with a high uranium content is sent to a hold-tank in the sump-recovery area and is then returned to the extraction stage. Settled sands and sludge are drawn off and separated from the raffinate by filtration through a box filter.

A quantity of sulfuric acid, equivalent to the combined nitrate present, is added to the raffinate slurry to free the combined nitrates. The slurry is then passed through a forced-circulation evaporator, and nitric acid is flashed in a vertical flash-chamber. The nitric acid from the evaporator (30 wt % HNO_3) is sent to the fractionating column in the nitric-acid recovery area. The temperature and viscosity of the bottoms are the controlling factors in the evaporation step as they indicate the completeness of evaporation. Between 75% to 80% of the nitric acid contained in the raffinate is recovered for re-use.

The evaporator bottoms—essentially molten salts—must be further processed before they may be discarded. The bottoms are pumped into one of two mild-steel neutralization tanks; these are filled with the required amount of dolomitic hydrate slurry, to neutralize a certain volume of evaporator bottoms. The tanks are operated in parallel, one receiving evaporator bottoms while the other is discharging to a rotary vacuum-filter.

The filter cake is collected in a bin and periodically removed by truck to a storage area for residue. The filtrate goes to monitoring tanks where it is analysed for uranium, arsenic and iron before discharge into Lake Ontario. At this stage the filtrate satisfies the requirements for discharge for effluent wastes that have been set up by the International Commission for the Control of Boundary Waters.

NITRIC ACID RECOVERY

The main streams from which recoveries are made are:

Area	Type
Digestion	Digestion fumes
Boildown and denitration	(a) Denitration fumes (b) Liquors from the denitration scrubber
Raffinate treatment	Overheads from the raffinate evaporator

Nitric acid is recovered by (i) concentration and (ii) absorption. Concentration is carried out in a fractionator on streams which contain either liquid nitric acid or nitric-acid vapour. Absorption is carried out on gaseous streams containing gaseous NO and NO_2. The concentration section produces a 55 wt % nitric acid and the absorption section produces a 40 wt % nitric acid.

Absorption

The gaseous streams produced from the denitration and digestion operations contain NO and NO_2 of sufficient quantity to warrant their recovery. These streams are first scrubbed in their respective areas. The absorption system is designed to receive these gases which are of the approximate composition shown in Table 4.

There are two principal reactions involved in the absorption of nitrogen oxides to form nitric acid. NO is first oxidized to NO_2; this is a comparatively slow gas-phase reaction. Then NO_2 is absorbed in water to form HNO_3 and NO. The NO formed in the latter reaction must again be oxidized to NO_2. Both the liquid-phase absorption of NO_2 in water and the gas-phase oxidization of NO are favoured by low temperatures.

The gas streams from digestion and denitration are drawn by two turbine blowers into the oxidation section built into the bottom of the absorber. A small amount of air is bled into the system to provide oxygen for oxidation of the NO. The gases stay long enough in the oxidation system to become oxidized from an estimated 30%–40% NO_2 to 85%–90% of the total ($NO + NO_2$) content. The fumes pass upward through a falling spray of nitric acid which removes about 22 kw (75,000 BTU per hour) of the heat evolved during the oxidation of NO to NO_2 and lowers the temperature of the gases to 38°C (100°F).

Fumes leaving the oxidation section pass upward through the absorption section of the tower. The absorption section is composed of several bubble-cap trays, some of which are provided with cooling coils. These cooling coils, through which cooling water is circulated, remove about 47 kw (160,000 BTU per hour) of heat evolved by the chemical reactions.

Trace quantities of chlorides, introduced into the absorber with the reflux or by way of the feed gases, accumulate at an intermediate point in the absorber. The chlorides apparently exist in the liquid phase as nitrosylchloride and are usually found at their greatest concentration where the acid strength is between 22 and 23 wt %. Neglect in removing this chloride could result in an excess of corrosion in the absorber at the zone of high chloride concentration. Facilities for oxidizing chlorine, which will be discussed later, are capable of handling a purge stream from the absorber. Several bleed-off points have been provided.

Fractionation

The sulfuric acid " springing ", and the evaporation of waste raffinates results in the evolution of considerable quantities of nitric acid and water in the vapour form. These vapours are efficiently concentrated in a conventional bubble-tray fractionating tower. This tower is designed to handle:

(*i*) overheads from the raffinate evaporator at 140°C (285°F), being approximately 30 wt % HNO_3;

(*ii*) dilute acid condensate formed during the scrubbing of denitration gases at 40°C (105°F), 34 wt % nitric acid;

(*iii*) miscellaneous liquid streams of nitric acid such as sump acid and material that does not meet specification.

All these streams are fed directly into the fractionator, which is operated at about 150 mm Hg absolute pressure. About 99% of the nitric acid in these feed streams is recovered as a bottoms product of 55 wt % nitric acid.

Chloride Removal

Chlorides are removed from the nitric acid by treating it with ozone. The stream from the nitric-acid fractionator is taken off at approximately the 20 wt % HNO_3 level at a temperature of 63°C (146°F) and the acid stream from the absorber is taken at the 23% level. Chlorides contained in the acid are oxidized by ozone to chlorine. Ozone is generated in three industrial-type, electrical discharge generators from dried instrument air. The generators are used simultaneously to produce a total of 27 kg (60 lb) of ozone per day. The air stream emerging from the generators will contain about 1 wt % ozone. This ozone-air mixture is then distributed by diffusion into the bottom of the ozonation tank. The chlorine formed is carried by the air and discharged to the atmosphere through a central stack. The ozone facilities are capable of removing approximately 6 kg (14 lb) of chloride per day.

Sump Recovery

The sump-recovery area is provided (i) to process various waste streams and off-specification liquors for the recovery of uranium and (ii) to monitor all waste liquors leaving the plant for uranium content.

The two main liquid wastes which are treated in the sump-recovery area are the carbonate washes from the solvent-extraction treatment, and the various floor sump collections from the digestion, extraction, boildown, denitration and raffinate areas. A separate floor sump is installed in the solvent-extraction area because the collected waste in this area usually contains solvent. These wastes are passed to a solvent-separation system where the aqueous and inorganic phases are separated. The carbonate-waste solutions are acidified with nitric acid to a pH of less than four in order to decompose soluble uranyl carbonate. The uranium and other impurities are then precipitated from solution by neutralization with ammonia. The slurry is filtered, the uranium-containing cake is re-dissolved in nitric acid, and returned to the digestion area.

The filtrate is sent to the monitoring tanks, and after checking for radioactivity is discharged into Lake Ontario.

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