

DIVISION OF  
ORE DRESSING AND  
METALLURGY



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O T T A W A February 10th, 1933.

REPORT OF INVESTIGATIONS

Section of Hydrometallurgy and Electrochemistry

Division of Ore Dressing and Metallurgy

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Report No. 478

Methods of Treating Great Bear Lake  
Pitchblende for Extraction of Radium

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Methods of Treating Great Bear Lake  
Pitchblende for Extraction of Radium.

By

R. J. Traill

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Introduction -

In the "Report of Investigations" of this Division for last year a preliminary report was included outlining the initial experimental work carried out with the purpose of selecting a process suitable to the treatment of the pitchblende from the above area for the extraction of radium.

The following report is a continuation of that work embracing experiments on a larger scale. Minor alterations

in the procedure suggested in the former report were found to be necessary in order to minimize certain losses of radium that became apparent in the larger scale tests. A 20 ton shipment, representing ore taken from several pits, was submitted by the Eldorado Gold Mines Ltd. for the purpose of determining the best methods of preparing the ore for treatment, and for determining the suitability of the suggested process for the extraction of radium from representative samples of the ore.

From an examination of the pit shipments it developed that two distinct types of ore occur in the deposit sufficiently dissimilar in chemical composition to require separate methods of treatment for the most efficient extraction of radium.

Two methods of treatment are therefore suggested in the following text, with results indicating satisfactory extraction of radium combined with a minimum of operation. These methods are designated as Procedure I for the treatment of the high silica gangue type pitchblende and Procedure II for the carbonate-berite-gangue type pitchblende which also contains silver.



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Large Laboratory Test Unit for Radium Extraction -

Due to the excessively corrosive action of the solutions, chemical acid proof stoneware was selected as the most suitable material for plant construction. For the first few tests wooden precipitation tanks were tried but were replaced by stoneware on account of their tendency to absorb fine precipitate and their failure to withstand the action of the hot acid solutions of the ore. Hard rubber rotary gear pumps connected to  $\frac{1}{2}$  H.P. motors were employed for transferring solutions through hard rubber pipes, the temperature of solutions being kept below 55°C.

The accompanying photograph illustrates the setup of the plant used. The leaching tank (upper left) is of 15 gallon capacity and is heated by a steam line entering through cover. Agitation is maintained by means of a stoneware agitator. The cover also has a charge opening, and another opening is connected to a suction fan for the purpose of drawing off acid and other fumes.

Underneath the leaching tank is a suction type stoneware filter, with a 15-gallon capacity upper section and a 25 gallon capacity lower section. The filter medium comprises blue asbestos cloth over a porous stoneware plate. Suction is provided by a Crowell rotary pump.

Below the filter is a rectangular receiving tank used principally for cooling the leach filtrate before pumping through the hard rubber pump.

The large upper tanks are the precipitating tanks each having a capacity of 75 gallons and provided with suitable agitators, and the lower tanks are the radium-free filtrate receiving tanks of equal capacity.

A 12 inch Buchner type porcelain funnel with filter paper is used as the filtering medium between the upper and lower tanks.

The leaching capacity of this unit is equal to a

10 Kilogram (22 pound) charge of 55 per cent  $U_3O_8$  ore or a 15 Kilogram (33 pound) charge of 35 - 37 per cent  $U_3O_8$  ore.

Preparation of Ore -

In preparing the ore for treatment two important factors have to be considered. Firstly, a minimum amount of fines is desirable to prevent a slow filtration condition and secondly, dusting has to be eliminated as completely as possible to minimize the loss of valuable material and more important, to minimize the health hazards to workmen from inhaling the fine dust.

Investigation into the treatment of the ore showed that for quick leaching, the ore should be crushed and ground to pass a 35 mesh screen; for good filtration, a minimum of fines was desirable so that the problem presented in its preparation was to determine the methods of crushing and grinding that would fulfil these conditions.

The treatment method also showed that roasting was necessary for the pitchblende containing the carbonate gangue minerals, to prevent excessive effervescence when brought into contact with the hot acid.

It was found that the ore should be crushed to about 4 mesh, the carbonate-type pitchblende roasted at this size and the final grinding done in a rod mill to give a 35 mesh product. Grinding in a rod mill gave the more desirable product, (more uniform with less fines) than any other method investigated.

Wet grinding was considered but was not deemed necessary nor economical for a small plant where the operation would be intermittent. The ore would have to be crushed and roasted in the dry state and provision made for taking care of the dust problem for these operations. Accessory equipment

such as classifiers, thickeners, filters, etc., would be required for wet grinding and the loss in fine slime would probably be greater than the dust loss of a dry grinding plant. Efficient dust collecting systems are now available for dry grinding operations.

Tests were conducted on the various lots comprising the 20-ton shipment, brought out from the property in the fall of 1931, and received at the Ore Dressing and Metallurgical laboratories for the purpose of determining the methods to be employed in the preparation of the ore and obtaining therefrom representative samples for the treatment investigation.

The various lots were crushed in a jaw crusher to about  $1\frac{1}{2}$  inch size, and in rolls to about  $\frac{1}{2}$  inch size. In the case of the carbonate gangue pitchblende, a 4-mesh roll product was found a satisfactory size for roasting. Batch charges were roasted in a muffle furnace for one hour with the temperature maintained at 750°C. A satisfactory product when ground to 35 mesh was obtained for leaching. Sufficient of this type of ore was not available to determine whether the dust loss from a multiple-hearth furnace with revolving rabble arms, or from a revolving kiln type of furnace, would be excessive and give the same satisfactory results.

Grinding tests on the 4-inch calcined product and the  $\frac{1}{2}$  inch roll product were carried out using the following grinding mills:

No. 0090 Raymond Pulverizer in circuit with 35 mesh Hummer screen on the 4 mesh calcined and  $\frac{1}{2}$  inch roll product.

Traylor 4' free screening ball mill fitted with 40 mesh ton-cap screen and in circuit with 35 mesh Moto-Vibro screen on the  $\frac{1}{2}$  inch roll products.

Marcy 3' x 6' open door discharge rod mill in circuit with 35 mesh Moto-Vibro screen, on the  $\frac{1}{2}$  inch roll product. Feed rate - 2040 lbs. per hour. Rod charge - 4013 lbs.

The following comparative screen tests give the

grinding obtained from the three types of grinding mills on the 1/2" roll product:

<u>Mesh</u>	<u>Pulverizer</u>	<u>Ball Mill</u>	<u>Rod Mill</u>
+35	All thru	0.1%	1.4%
-35 +48	2.7%	6.1%	7.2%
-48 +65	9.4%	23.4%	34.5%
-65 +100	11.8%	4.8%	12.8%
-100 +150	8.5%	10.7%	2.7%
-150 +200	6.8%	6.6%	8.0%
-200	61.4%	46.3%	34.0%

The hammer consumption for the pulverizer was 3 lbs. per ton.

The ball consumption for the ball mill was 3 lbs. per ton.

The rod consumption for the rod mill was 1 lb. per ton.

The results of the above tests show rod mill grinding gives the more desirable product. By decreasing the rod charge and carrying a greater <sup>circ</sup> insulating load the results given in the screen test can be improved upon.

The flow sheet recommended for the preparation of the pitchblende ore, is as follows:—Crushing in a jaw crusher and rolls in circuit with 4 mesh screen  
Calcining of the 4 mesh product in case of the carbonate gangue pitchblende in a suitable roasting furnace.

Grinding the calcines or the 4-mesh ore in a rod mill in circuit with a 35 mesh screen.

Provision made for efficient dust collecting system to take care of the dust from all operations.

Analysis of the Lots from 20-ton shipment:

The following table gives the analysis of the various lots comprising the 20-ton shipment.

	Vein 1 Pit 1	Vein 2 Pit 1	Veins Pits 2-6	Vein 2 Pit 9	Vein 2 Pit 9
Uranium - U	37.82	33.92	35.19	36.96	27.47
$U_3O_8$	44.6	44.0	41.50	45.94	32.40
Lead - Pb	7.89	8.14	7.23	10.62	6.88
Iron - Fe	2.21	2.06	2.26	2.37	7.00
Copper - Cu	0.85	0.82	0.80	2.80	2.90
Manganese - Mn	0.18	0.17	0.17	4.90	9.05
Nickel - Ni	nil	nil	nil	nil	nil
Cobalt - Co	0.26	0.35	0.22	0.43	0.16
Antimony - Sb	0.13	0.06	0.07	0.15	0.06
Barite - $BaSO_4$	trace	nil	nil	2.18	2.10
Silica - $SiO_2$	34.10	31.50	35.90	1.76	3.26
Arsenic - As	0.23	0.25	0.18	0.47	0.44
Sulphur - S	1.31	1.05	0.83	2.20	3.01
Lime - CaO	0.95	0.90	0.75	3.00	3.65
Magnesia - MgO	0.67	0.47	0.41	0.54	0.68
Alumina - $Al_2O_3$	1.00	1.75	1.37	1.03	1.16
Water - $H_2O$	1.20	1.95	1.66	1.64	2.10
Alkalies - $Na_2O+K_2O$	1.30	1.36	1.45	1.81	2.12
Phosphorus - P	0.074	0.17	0.15	0.17	0.17
Molybdenite - $MoS_2$	0.23	0.10	0.17	0.10	trace
Zinc - Zn	trace	trace	trace	0.22	0.10
Carbon dioxide - $CO_2$	1.67	1.50	1.23	7.72	11.72
Silver - Ag ounces per ton	4.20	5.71	10.97	301.67	360.98
Sp. Gravity	4.32	4.19	4.08	4.75	4.38

It will be noted in the above table that there are two samples from Vein 2 pit 9. The reason for this is that on the material taken from this pit an attempt was made before shipment to cob out high grade pitchblende ore and high grade silver ore separately.



Treatment of High Silica Type Pitchblende

Procedure I.

The initial larger scale tests on this type ore indicated on examination of residues that satisfactory radium extractions were obtainable by the procedure suggested and described in the report for 1931.

Minor difficulties such as oxidation, filtration and washing had to be worked out to improve extraction and to carry the primary operations through in a minimum of time.

The procedure formerly suggested embraced washing the residue with brine to remove lead chloride therefrom, combining these washings with the main filtrate and allowing the lead chloride to precipitate out in the diluted solution. The lead chloride was then separated by filtration and the filtrate treated with barium chloride and sodium sulphate for precipitation of radium. In this procedure it was found that the lead chloride showed a decidedly high radioactivity due to the presence of elemental radium. This radium content, it was proved, could be recovered by re-leaching the lead chloride with brine, indicating that some element in solution was precipitated by dilution and had the property of carrying with it important amounts of radium. The element responsible appeared to be principally silica, probably present as a soluble product in the hot acid solution, but becoming insoluble on cooling. The procedure, therefore, was altered to overcome this condition. Instead of using a brine wash on the residue, hot water was substituted, the amount of lead chloride contained in the residue being readily removed by this means. The washings were combined with the main filtrate and instead of permitting the lead chloride to precipitate and separate as previously, the precipitation of the radium by the addition of barium chloride and sodium sulphate was made directly, the whole being agitated for a total of 24 hours. A precipitate

was thus obtained consisting of radium-bearing sulphate and lead chloride. This precipitate was next filtered off and treated with a strong brine solution whereby the lead chloride was dissolved and the radium-barium sulphate remained insoluble.

The brine solution upon dilution gave a lead chloride comparatively free from radium. This altered procedure saves the loss of radium occurring in the lead chloride, or saves a secondary treatment of the lead chloride for recovery of contained radium and in addition reduces the time for the first step of the process namely concentration of the radium by a full day.

Procedure I therefore may be briefly described as follows:—

The ore ground to 35 mesh is leached with 15°Be hydrochloric acid, (low in sulphate content,) for three hours at a temperature above 90°C, the quantity of acid used varying with the grade of ore. A solution of sodium nitrate is then added in small amounts at short intervals so that oxidation will not be too rapid nor frothing too excessive. The sodium nitrate has the effect of oxidizing and thereby making more readily soluble the highly refractory uranous oxide ( $UO_2$ ) content of the ore.

The  $UO_2$  content in these silica pitchblende ores apparently varies distinctly, ranging in the ratio of  $3\frac{1}{2}$  to 4 parts  $UO_2$  for each part  $UO_3$ , with the higher  $UO_2$  ratio following higher silica content.

The oxidation operation requires about one and half hours. With the leach completed the residuum is separated by filtration. Filtration should be carried out while the liquor is hot, as lead chloride separates out rapidly with cooling and makes filtration more difficult. The residue is well washed with hot water, the washings and main leach solution are combined and treated with measured quantities of barium chloride and sodium sulphate while warm, to precipitate

the radium with barium as sulphates. Agitation for about 24 hours insures practically complete precipitation of radium, and after allowing the precipitate to settle, it is separated by filtration and washed with acidulated water to remove base metal salts. The filtrate containing uranium and other metal chlorides is treated for recovery of uranium. The lead chloride + radium-barium sulphate precipitate is now treated with a hot solution of brine, whereby the lead chloride is dissolved, the radium-barium sulphate remaining insoluble and being collected on a filter. This precipitate constitutes the radium concentrate and is sent to the refining plant for final recovery of radium.

The above operations produce a concentrate can be readily completed in 4 days.

The accompanying flow sheet (I) illustrates the various steps of this procedure.

Flow Sheet I  
for High silica type pitchblende  
Results of Tests

Numerous tests were made in the manner described with results as shown in the following examples:-

Sample of first shipments of ore.

Composition:-  $U_3O_8$  - 56.8%;  $SiO_2$  - 19.32%; S - 0.86%.

Ore charge kilograms	Radium Content milligrammes	Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.637	2910	0.106	93.5
10	1.637	2486	0.0296	98.2
10	1.637	2535	0.0513	96.8

Sample of Vein #1 Pit #1 pitchblende ore, part of 20 ton shipment.  
Composition:-  $U_3O_8$  - 44.6%;  $SiO_2$  - 34.1%; S - 1.31%.

Ore charge kilograms	Radium Content milligrammes	Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.2854	3900	0.0506	96

Sample of Vein #2 Pits 2 to 6 pitchblende, part of 20 ton shipment.  
Composition:  $U_3O_8$  = 41.8%;  $SiO_2$  = 53.9%; S = 0.88%.

Ore charge kilogrammes	Radium Content milligrammes	Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.196	4240	0.02	98.3

Included in the 20 ton lot was a 2500 pound shipment from Vein #2 Pit #1.

This ore has the same general appearance and chemical composition as those above, but on test does not show extractions quite as satisfactory by direct leaching. The reason for this cannot at present be satisfactorily stated as a complete analysis of the ore is not available, and time has not permitted to make a definite investigation of the problem.

Direct leaching by the procedure described above shows an average extraction of about 60 per cent of the radium, the remainder being found in the residue. The residue contains practically no uranium and the radium is in a form that is insoluble in acids. Barium would naturally be suspected as the cause of the retention of radium in the residue but this element is present in an exceedingly small amount and may therefore be eliminated as the disturbing factor.

As a means of increasing the radium extraction, retreatment of the residue is the only plan that can be suggested for the present, and the following method has been used with good results.

The residue is heated with a solution of soda ash for 3 hours with agitation, diluted with water and allowed to settle. The clear solution is then syphoned off and the residue transferred to a pressure filter and washed with water. The washed residue cake is then treated with 1-1 hydrochloric acid (low in  $SO_2$  content) and after thorough agitation, the insoluble is separated by filtration. The filtrate contains the radium which may then be precipitated by the addition of barium chloride and sodium sulphate or sulphuric acid.

Filtration of both the alkaline and acid solutions is usually slow and washing is likewise tedious and time consuming.

By this double treatment, extractions have been increased to over 95 per cent. The following examples are typical of the results obtained:

Sample of Vein #2 Pit #1 pitchblende ore.

Composition:  $U_3O_8$  - 44.0%;  $PbO_2$  - 31.5%; S - 1.05.

Ore charge kilogrammes	Radium Content milligrammes	Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.268	3650	.2046	83.9
By retreatment of residue		3655	.0438	96.5
10	1.268	3760	.2056	83.8
By retreatment of residue		3047	.0457	96.5
10	1.268	3770	.2025	84.0
By retreatment of residue		3016	.092	92.7
10	1.268	3776	.34	73.2
By retreatment of residue		3227	.05	97.6

In all of the tests made the uranium extraction was higher than the radium extraction, the majority of the tests showing 89.9 per cent extraction.

The main filtrates, after precipitation and separation of the radium barium sulphate and the lead chloride, contained an average of 0.00145 milligrammes radium, or less than 0.10 per cent of the total radium.

The separated lead chloride from the brine solution, representing 70 - 85 per cent of the total lead content of the ore, contained an average of 0.00057 milligrammes radium, or less than 0.04 per cent of the total radium content, while the brine solutions, after separation of the lead chloride, contained an average of 0.005 milligrammes or approximately 0.40% of the total radium. The concentrates contained 86-87 per cent of the total radium content in concentrations varying from 1 part radium in 90,000 to 1 part in 125,000.

Procedure II - Carbonate - barite - silver type pitchblende.

The twenty ton shipment from the Eldorado property included two lots of this type of ore from the same pit.

The partial analysis of these lots is shown in the forepart of this report (Preparation of Ore). Initial laboratory tests on this type of ore showed that, by direct leaching, the radium content would be divided between the insoluble residue and the leach solution, the greater proportion being held in the insoluble residue by reason of the presence of barium sulphate. In addition to this, direct leaching with acid was attended with difficulties on account of the high carbonate content of the ore causing excessive frothing. The addition of acid to the ore in the most careful manner proved unsuccessful due to an apparently delayed reaction of the rhodochrosite with the acid, which caused an overflowing of the charge in the leaching tank.

The difficulty was eventually overcome by roasting the ore at a temperature of 750°C - 800°C with good access of air, whereby the carbonates were materially broken up or decomposed. Acid leaching could then be carried out with complete safety.

Leaching with hydrochloric acid (13°Be), the radium remained in the insoluble residue with the silica, barium, silver etc., hot water washing removing practically all of the lead. The presence of a small amount of sulphate, formed during the roasting (or added) insures almost complete precipitation of radium in the residue. The filtrate contains the uranium, lead chloride and some silver chloride. When filtration of the leach is carried out hot, there is a greater amount of silver chloride carried to the filtrate, than when the leach is allowed to cool before filtration. The latter procedure is therefore recommended, the leaching charge being allowed to cool and settle, the clear liquor syphoned off through the filter and the residue finally

transferred to the filter with hot water and thoroughly washed.

The removal of silver from the residue would appear to be the next logical step. This is readily accomplished by leaching with sodium cyanide solution, the silver, present for the most part in the form of chloride, being easily soluble. The silver in solution may be recovered by any of the standard processes such as precipitation by sodium sulphide, aluminum or zinc. The silver free residue is next treated with a solution of sodium carbonate at boiling temperature and with continuous agitation for several hours, whereby the radium-barium sulphates are changed to carbonates. Filtration and careful washing eliminate the excess alkali and the sodium sulphate.

The residue of silica and carbonates is then treated with hydrochloric acid, the carbonates dissolving to chlorides, and the silica remaining insoluble is eliminated by filtration.

To the filtrate of the chlorides sodium sulphate is added in excess to precipitate the radium with the barium, the precipitate constituting the radium concentrate ready for refining. Preliminary tests following this procedure indicated that 95 per cent of the total radium content of the ore could be extracted as radium barium sulphate.

Large scale tests using 10 kilograms (22 pounds) samples were <sup>made</sup> run with equally satisfactory results as shown below.

The equipment used in procedure II was as follows.

The ore was roasted in a gas fired muffle hearth type furnace at 750 - 800°C for about an hour. For acid leaching of the roasted ore and filtration of the leach, similar equipment to that used in Procedure I was employed. Cyanidation of the residue was carried out in porcelain pebble jars containing a small quantity of pebbles the jars being rotated. Pressure filtration was used for separation of

residue and cyanide solution. Conversion of the sulphates to carbonates by soda ash was accomplished in equipment similar to that employed in the primary leach, filtration being done in a pressure filter. Final acid leaching was done in glass for convenience, but would ordinarily be done in stoneware.

The low silica content of this type of ore assists in permitting quick filtering at all stages.

The various steps in the recommended procedure for ores of this type are shown in flow sheet II.

- Flowsheet II -

Typical examples of results obtained by this procedure are as follows:—

Roasted Ore:—  $U_3O_8$  - 51.15%; Ag - 359.9 oss./ton;  $BaSO_4$  - 3.00%.

Ore charge kilograms	Radium Content milligrammes	Final Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.475	692	.0545	96.3
10	1.475	610	.0484	96.8
10	1.475	591	.0355	97.5

Roasted Ore:—  $U_3O_8$  - 42.05%; Ag - 223.6 oss./ton;  $BaSO_4$  - 5.10%;  
 $SiO_2$  - 18.7%.

Ore charge kilograms	Radium Content milligrammes	Final Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.21	2160	.0776	93.6

Roasted Ore:—  $U_3O_8$  - 50.5%; Ag - 342.6 oss./ton;  $BaSO_4$  - 2.75%;  
 $SiO_2$  - 2.30%.

Ore charge kilograms	Radium Content milligrammes	Final Residue grammes	Radium Content milligrammes	Extraction per cent
10	1.456	890	.027	98.1
10	1.456	208	.0236	98.4



Roasted Ore: -  $U_3O_8$  = 38.8%; Ag = 380.9 oz./ton;  $BaSO_4$  = 7.70%;  
 $SiO_2$  = 6.55%.

Ore charge kilogrammes	Radium Content milligrammes	Final Residue grammes	Radium Content milligrammes	Extraction percent
10	1.118	997	.0368	96.7

The uranium extractions in all cases were well above 99 per cent.

The uranium filtrates varied in total radium content between 0.003 and 0.015 milligrammes, the lead chloride between 0.004 and 0.02 milligramme, the sodium cyanide solutions between 0.00004 and 0.0025 milligramme, the sodium carbonate solutions between 0.0002 and 0.002 milligramme, and the final acid filtrate from the radium barium sulphate precipitation averaged 0.00005 milligramme.

The total radium losses in these solutions was in all tests under 2 per cent. The silver recoveries from the cyanide solution varied from 84 to 93 per cent of the total silver content of the ore. The silver was here recovered by sodium sulphide precipitation and reduction of the silver sulphide to metallic silver. The radium barium concentrates varied in grade being governed by the barium content of the ore. All the barium in solution must be precipitated to obtain complete precipitation of the radium, and so the higher the barium content in the ore the lower the grade of concentrate obtainable and this is reflected further in the crystallization laboratory where increased fractionations will be required.

The operations entailed in this method of procedure should not require more than 8 to 10 days to produce a concentrate of radium, ready for refining.

#### Refining of Radium-Barium Sulphate.

In the treatment of pitchblende for the production of radium two main steps may be said to be involved, first the concentration of the radium and second the refining of the concentrate to obtain radium salts.

The first of these two steps, relating to the ores

under consideration, has been accomplished by the methods shown above, and a concentrate of radium in barium sulphate has been obtained.

The refining of this concentrate has not been carried out in this present investigation, mainly because the method used is already a well established practice, and was first proposed and used by Madame Curie some thirty years ago and has not been improved upon in any marked degree.

The refining of the concentrate entails mainly the separation of radium and barium and the only economical method known is by fractional crystallization of the soluble salts of the two elements.

To obtain the soluble salts the radium-barium sulphate is converted to carbonate by boiling with sodium carbonate. The soluble sulphates and excess alkali are leached out and the residue thoroughly washed with sulphate free water.

The carbonates in the residue are then leached with C. P. Hydrochloric Acid, the chloride solution filtered, and the insoluble washed and returned for retreatment with sodium carbonate to convert any remaining sulphate to carbonate and thence to chloride.

The chloride solution sometimes contains appreciable quantities of lead which are removed by passing hydrogen sulphide gas through the solution and the sulphide is separated by filtration. Sometimes in presence of other impurities it is advisable to pass the hydrogen sulphide into an ammoniacal solution of the chlorides.

A departure from the above procedure was made by the U. S. Bureau of Mines investigators in their work on refining the radium concentrate obtained from the carnotite ores. The method consisted of reducing the barium sulphate by means of charcoal to barium sulphide, the radium also changing to sulphide. The sulphides were then leached with

hydrochloric acid, the solution filtered and the unconverted sulphates retreated.

The process, however, has not been adopted elsewhere and the original method of Curie is generally adhered to.

The solution of the chlorides is now evaporated to the crystallizing point. Radium chloride is less soluble than barium chloride and concentrates in the crystal fractions. This insolubility is greater in acid solutions than in neutral, and crystallizations are therefore carried out in acid solutions.

The crystal fraction of a chloride solution contains approximately four times as much radium as remains in the mother liquor.

These first crystals are now put into solution, the solution brought to the crystallizing point and a second crop of crystals obtained much higher in radium content. This scheme is continued until the concentration has reached about 50 milligrams radium element per kilogram, at which point the chlorides are usually converted to bromides, the bromide of radium being still less soluble than the chloride, and the fractionations continued in hydrobromic acid.

The mother liquors are all treated in the same way, the crystal fractions being put into the system at the most convenient points. The system of crystallization is established according to the ratio of radium to barium in the concentrate obtained from the plant. The final radium bromide is tubed and stored in lead lined compartments, and checked several times for radium content. A purity of 95-98 per cent is usually called for. A careful account of the radium content of all liquors, precipitates and crystals is maintained to determine the efficiency of the various steps.

#### Recovery of Uranium

No attempt has been made so far in this investigation to conduct large scale tests on the recovery of uranium, but small scale tests indicate that this phase should present no serious difficulty.

Methods already established are quite applicable and

the general scheme may be briefly outlined as follows.

The main acid leach filtrate carries, as shown in test results, practically all of the uranium in acid chloride solution, together with iron copper manganese and other base metals.

Most uranium compounds are soluble in solutions of alkaline carbonates and the methods commonly employed use this as the basis of separation from the other metals present.

Treatment of the acid leach filtrate with excess sodium carbonate precipitates most of the base metals, the uranium remaining in solution as sodium uranyl carbonate. The precipitate of base metals is separated by filtration and the filtrate is neutralized with acid, a yellow precipitate consisting of sodium uranate and uranyl carbonate being formed, which is soluble in excess of acid.

This yellow precipitate may be filtered off and the small amount of unprecipitated uranium remaining in solution recovered by addition of caustic soda or the main solution may be carried to the acid condition and all of the uranium precipitated as sodium uranate giving an orange coloured compound.

The procedure is governed by the nature of the uranium compound required and to some extent also by the impurities present.

The uranium compounds obtained are separated by filtration, washed and dried, and prepared for market according to the colour purity and grade required.

#### Analytical and Radioactivity Work.

The chemical analysis of ores and products in connection with this report was made by B. P. Coyne and H. L. Beer, of the Chemical Laboratory; assays for silver by L. Lutes and J. McCree of the Assay Laboratory. Determinations of radium in all products and stages of the methods were

performed by W. R. McClelland, details of which will be found attached to the report of this section.

Conclusions

<sup>Investigation</sup>  
~~Test work~~ on the present available pitchblendes from Great Bear Lake indicates that these ores can be readily treated for the recovery of radium.

The ores examined comprise two distinct types, differing widely in gangue-forming elements, one being a highly siliceous gangue pitchblende, and the other a carbonate-barite gangue pitchblende carrying silver.

No single process would appear to be economically suited to the treatment of the two ores for recovery of radium, and for reason of greater efficiency and better economic operation two separate processes are suggested.

Plant operation on the unit principle is advisable in working with such high-grade and valuable material, and, where for the most part similar chemicals and equipment are applicable to both processes, the two process plan should be quite feasible.

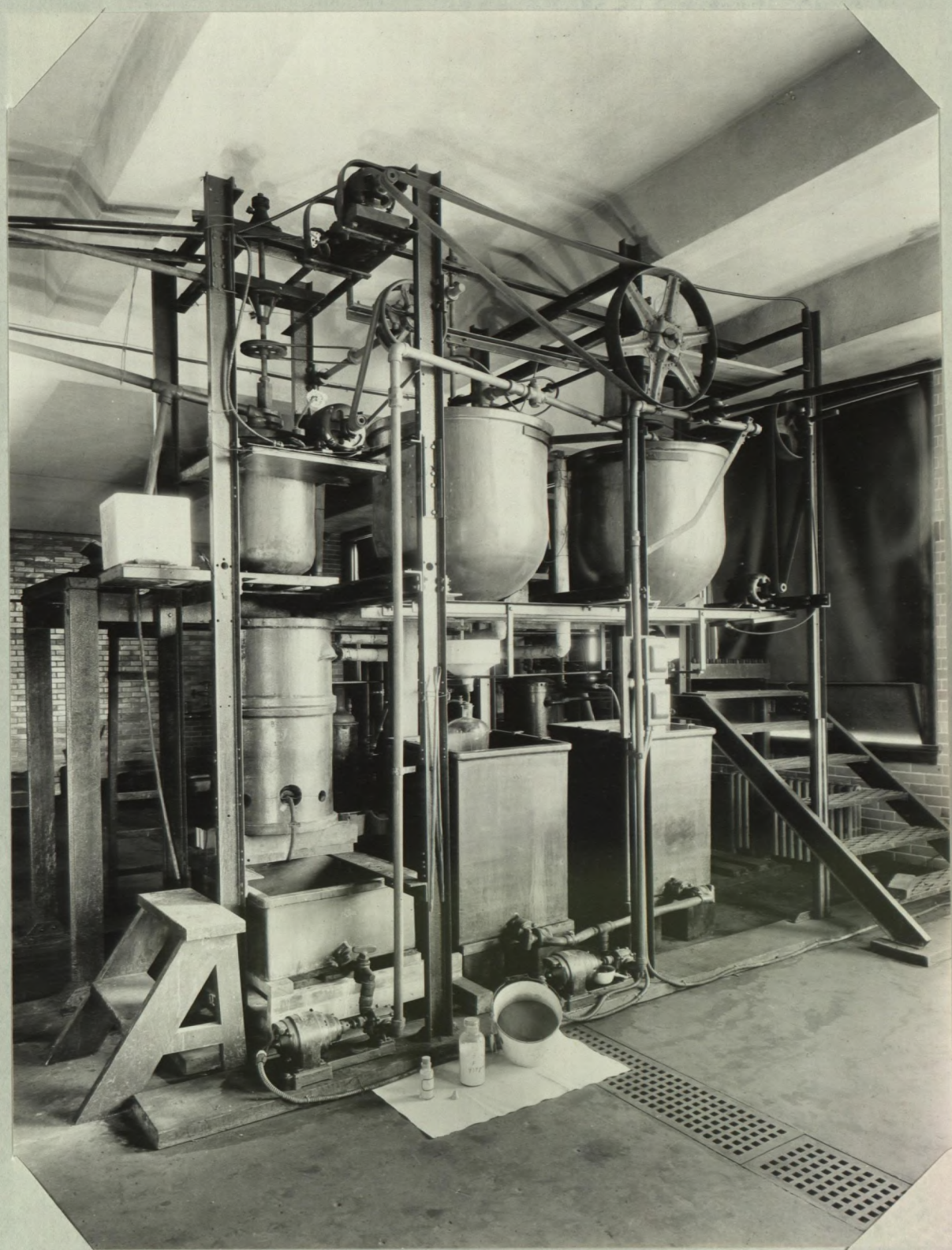
Units capable of treating 100 kilograms (220 pounds) ore per charge, based on present grade of ore, are suggested. Laboratory tests on a scale one-tenth this capacity have given satisfactory results, the uranium and radium extractions being well over 90 per cent in all tests, and all operations such as filtrations and washing have been performed without difficulty.

The procedure recommended for the high silica type ore is simple and direct, requiring a minimum of operations and time to produce a high-grade radium concentrate.

The procedure for the carbonate-barite-silver pitchblende, while involving a greater number of operations,

and longer time, is equally efficient and permits of readily <sup>a high</sup> recoverable <sup>ry of the</sup> silver <sup>Content</sup> values.

No attempt has been made to estimate costs of operation as this is dependent upon too many variables which <sup>with sufficient accuracy</sup> cannot be determined, on a laboratory-scale operation.



Pilot plant for investigation of the treatment of Great Bear Lake pitchblende for the extraction of radium. Note: in foreground, the charge of ore, 10 kilograms, in pail; the bottle of lead chloride recovered; the small button of silver recovered; the small bottle of crude radium salt.

PITCHBLENDE ORE

1/4" roasted at 750°C.

ROD MILL

ground to -35 mesh

AGITATOR

leached with hot HCL

FILTER

with hot water wash

FILTER CAKE

Residue containing  $SiO_2, Ra-BaSO_4, Ag$

AGITATOR

Na CN leach

FILTER

water wash

INSOLUBLE

DIGEST with  $Na_2CO_3$  dilute and settle

FILTER

wash free from sulphates

INSOLUBLE  $Ra-BaCO_3 + SiO_2$

LEACH with HCL

FILTER water wash

RESIDUE

Retreated if Radium content of value

HCL Solution containing  $Ra-BaCl_2$

$Na_2SO_4$  added agitate and settle

FILTER

water wash

PRECIPITATE of  $Ra-BaSO_4$

FILTRATE No value

Na CN solution containing Ag  
Ag precipitation and recovery

FILTRATE

Solution containing U, Pb, etc., chlorides

Cooled and settled

FILTER

with acid water wash

FILTER CAKE

Precipitate of  $PbCl_2, AgCl_2$

AGITATOR

Na Cl leach

FILTER

FILTER RESIDUE containing some Ra TO MAIN RESIDUE

FILTRATE

$Na_2S$  added to hot solution

FILTER

FILTER CAKE Precipitate of  $Ag_2S, PbS$

REFINERY for recovery of Ag

FILTRATE Brine solution containing  $PbCl_2$

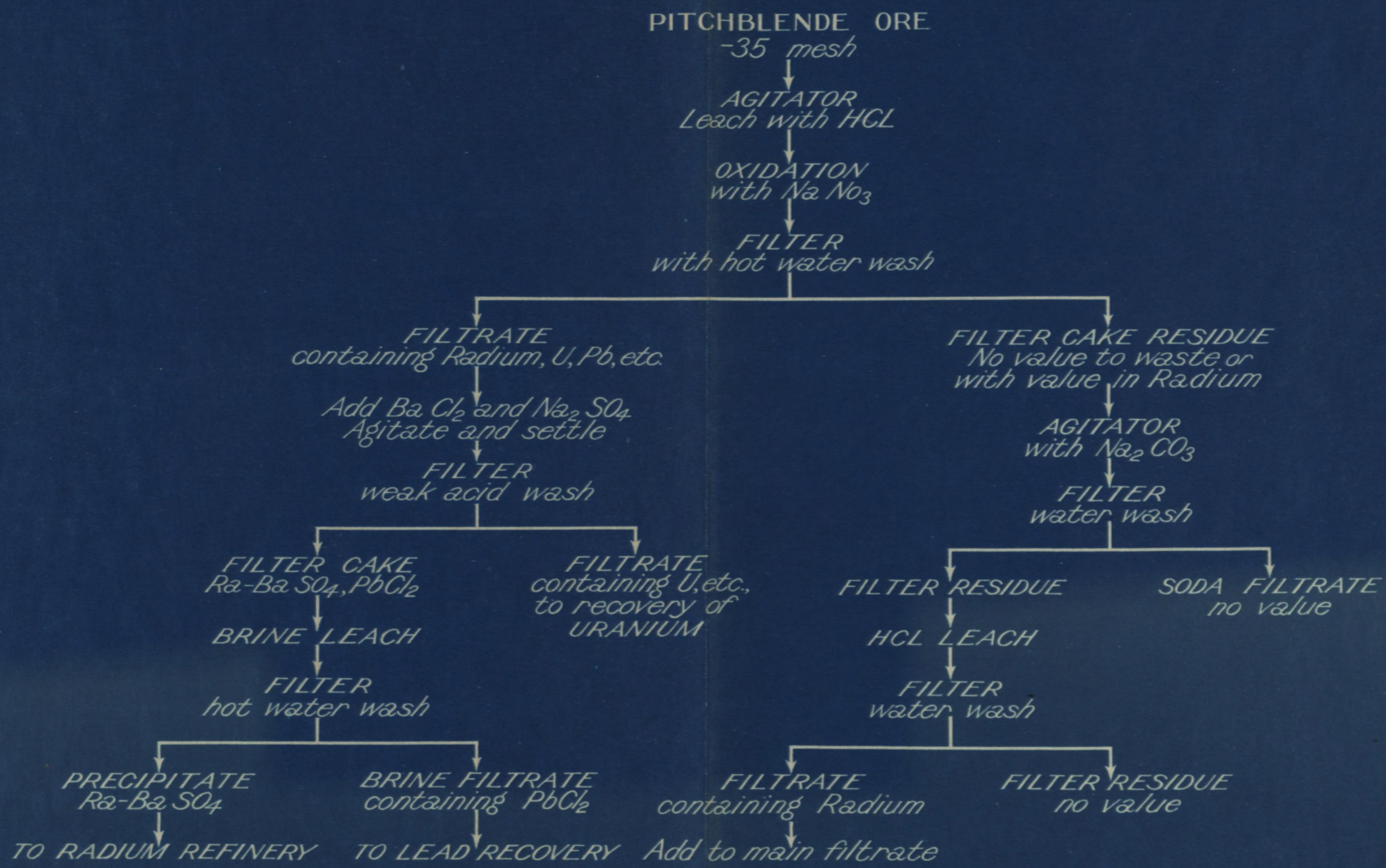
RECOVERY OF Pb

FILTRATE Solution containing U etc.

RECOVERY OF URANIUM

Flow-sheet for treatment of Carbonate-Silver Pitchblende Ore containing Barite





Flow-sheet for treatment of Silica Gangue Pitchblende Ore