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THE DETERMINATION OF U_3O_8 IN ORES AND SOLUTIONS

CELLULOSE COLUMN METHOD

by

F. T. Rabbitts, R. J. Guest, J. E. Jordan, E. D. Kornelsen

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Radioactivity Division

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GENERAL

The Analytical Section of the Radioactivity Division of the Mines Branch has been engaged since December, 1945, in testing and developing methods of analysis of uranium in ores and solutions. Two of the various methods tested were found to be suitable for routine analysis.

The first of these is the U.S. Bureau of Standards method modified by using the mercury cathode, described in Mines Branch Memorandum Series No. 103. This is an accurate method and can be applied to any type of uranium ore, but the procedure is long and the precision good only in the hands of an experienced analyst. Its chief disadvantage is that it is not suitable for a colorimetric determination at the end of the analysis because of the buildup of salts which tends to give cloudy solutions, resulting in too low a reading of the transmittancy.

The second method, described in this report, is a modification of the cellulose column method developed at the Chemical Research Laboratory, Teddington, England. The column method gives a considerable saving in time and reagents compared with the previous methods and yields

results of improved accuracy and precision. In addition it is applicable to any concentration of uranium in ores and solutions.

CELLULOSE COLUMN METHOD

The sample is brought into solution by a suitable method. If arsenic is absent, it is preferable to obtain a nitric acid solution free of chlorides and sulphates. An ether extraction of the uranyl nitrate is then performed in a cellulose column as described in CRL Report AE19. The ether in the extract is distilled off and the uranium remaining can be determined:

(1) colorimetrically by NaOH and hydrogen peroxide.

(2) volumetrically by Jones reductor and dichromate

(3) gravimetrically as the oxine precipitate

or (4) fluorimetrically.

With many ores it is necessary to eliminate arsenic before the column extraction as otherwise the recovery of uranium is not quantitative. Hydrobromic acid with hydrochloric acid and hydrazine hydrochloride are considered more suitable for eliminating arsenic than hydrogen sulphide since the separation can be accomplished by heating in the original beaker without a filtration. However a minimum amount of HBr should be used to avoid losses through spattering on evaporation.

Sulphates are removed largely by precipitation with carbonate free ammonium hydroxide and re-solution in nitric acid. If phosphates are present they can be complexed by iron. If insufficient iron is present in the sample, more is added as ferric nitrate solution.

With a large number of control samples the procedure can be

divided into several steps, one worker handling all the samples for his particular step in the analysis. The column method has been the standard method of chemical analysis for uranium in this laboratory for almost a year and has proven very satisfactory. However, further testing is in progress for possible additional modifications.

ANALYTICAL PROCEDURE

(a) Solution of Solid Samples and Arsenic Elimination

To the solid sample (-100 mesh) in a 250 ml. beaker add 10 ml. 1:1 HCl, cover and digest for 10-15 minutes. Remove cover and rinse. Add 10 ml. 1:1 H_2SO_4 and 5 ml. HNO_3 and evaporate to dryness finishing over small flame of gas burner. Avoid baking. Cool, add 5 ml. HCl, 5 ml. HBr and 5 ml. 5 per cent hydrazine hydrochloride. Fume carefully finishing over small gas flame. Cool, wash down sides of beaker and again fume over gas burner, but avoid baking. Add 5 ml. HNO_3 and 30 ml. water. Cover and boil 2-3 minutes. Filter on 1F paper into a 250 ml. beaker and wash well with hot 2 per cent HNO_3. Discard residue if white, otherwise retreat by suitable procedure such as bisulphate fusion.

(b) Treatment of Solution Samples

Measure out the clear sample with a 5 ml. burette. Use a 250 ml. beaker. Add 10 ml. 1:1 H_2SO_4, 5 ml. HCl, 5 ml. HBr and 5 ml. hydrazine hydrochloride (5 per cent). Fume carefully over burner. Cool, wash down sides and fume. Repeat and take almost to dryness. Moisten with HNO_3 and take to dryness. Repeat. Add 5 ml. HNO_3 plus 30 ml. water, cover and boil 2-3 minutes.

(c) Sulphate Removal and Ether Extraction

To the nitric acid solution from (a) or (b) add an excess of fresh ammonium hydroxide, stir, cover and boil 1-2 mins. Filter hot on 12.5 cm. 1F paper and wash 10-12 times with hot freshly prepared 2 per cent NH_4OH water. (If precipitate is large make a second NH_4OH pptn. If there is only a small amount of ferric hydroxide on the first pptn. redissolve in HNO_3 before filtering, add 5 ml. 20 per cent ferric nitrate and continue with the pptn. as usual.)

Test the final washings for sulphates with $BaCl_2$ solution acidified with HCl.

Allow the hydroxide ppt. to drain for 2-3 mins, remove paper and ppt. discarding paper free of hydroxide and place the remaining paper plus all of the ppt. in a 250 ml. beaker. Add 3-3 1/2 ml. HNO_3 and stir well to break up paper. Adjust liquid volume to 10 ml. if necessary. Add 2 ml. ether-HNO_3 plus dry pulp and stir well. Add more pulp with stirring till mixture is granular and slightly moist. Extract in column (NOTE 3), collecting about 150 ml. of ether. Add 15-20 ml. water, evaporate off ether on steam-bath and transfer to 250 ml. beaker with 3 or 4 small water washes.

(d) Destruction of Organic Matter and Colorimetric Determination

Add 10 ml. 1:1 H_2SO_4 to the beaker, place on hot plate for a few minutes and then fume over burner. Cool, wash sides of beaker, add 4 ml. HNO_3 and not more than 2ml. $HClO_4$, and fume strongly over burner. On low samples the green colour should disappear. Cool, wash sides and again fume over burner. Repeat and this time take to dryness. Add 1 or 2 drops 1:1 H_2SO_4, wash down sides with water and warm 1-2

mins. on hot plate to ensure complete solution. Cool under tap, add litmus paper and neutralize with 10 per cent NaOH, adding 5.5 ml. excess for final volume of 50 ml. Switch colorimeter on. Remove litmus washing well and add 15 drops Superoxol. Transfer to 50 ml. volumetric make to mark and mix well. Allow 20 minutes for colour development, mixing 3-4 times in this period to eliminate bubbles. Centrifuge, rinse absorption cell with solution, and then fill with sample. Clean windows carefully with Kleenex and read density against previously prepared reagent blank at 370 mu. and .1 slit. Have batteries at 1.250 density or better. Set circular slide rule and read off mg. From graph read per cent or grams per liter U_3O_8.

A Beckman DU spectrophotometer is used to determine the density. The cells are of Corex with a 10 mm. light path. The transmittancy curve for 50 ml. dilution is given in Fig. 2 shown on page 14.

NOTES

(a) Volumetric Determination of U_3O_8

This method is used for material containing over 1 per cent U_3O_8. It has already been described in detail in Memorandum Series No. 103, but a brief outline is included here.

After destroying organic matter in the column eluent with nitric, perchloric and sulphuric acids the sample is fumed at least three times to remove nitrates and perchlorates. It is then diluted to 100 ml. and the sulphuric acid content adjusted to 5 per cent. 100 ml. of 5 per cent H_2SO_4 is passed through a Jones reductor and discarded. Then the sample is passed through, collecting it in a 600 ml. beaker. The

reductor is washed with 200 ml. of 5 per cent sulphuric acid in 50 ml. portions. The combined sample and washings is aerated for 10 minutes, 25 ml. 5 per cent $FeCl_3$(lump) freshly-prepared plus 15 ml. H_3PO_4-H_2SO_4 mixture (1500:550) are added together with 8 drops of diphenylamine sulphonic acid indicator. The ferrous iron produced is then titrated carefully with 0.05N potassium dichromate.

(b) Gravimetric Determination of U_3O_8

(The following procedure is taken from "A Textbook of Quantitative Inorganic Analysis" by Arthur L. Vogel, Longman's.)

"The uranium should be in the form of uranyl nitrate or chloride in 1 or 2 per cent acetic acid solution (1), and the solution may contain up to 0.3g. of U. Add 5 g. of ammonium acetate, heat to boiling, and add slowly a four-fold excess of the oxine reagent (2). Digest on the water-bath for a short time and allow to cool. When cold, filter on a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash thoroughly with hot water until the excess of oxine has been removed (ferric chloride test), and then several times with cold water. Dry at 105 deg. to constant weight. Weight as $UO_2(C_9H_6ON)_2$, C_9H_7ON.

(1) If the solution contains mineral acid, almost neutralize with ammonia solution, add 5g. of ammonium acetate and then sufficient acetic acid to give a 1 to 2 per cent acid solution.

(2) The oxine reagent is prepared as follows:

Dissolve 3 g. of oxine in the minimum volume of glacial acetic acid, dilute to 100 ml. with water, add dilute ammonia solution dropwise until a permanent slight precipitate separates, and just dissolve the latter by the addition of a little dilute acetic acid."

(c) Fluorimetric Determination of U_3O_8

This method is particularly valuable for the accurate determination of very small amounts of U_3O_8. Preliminary development work is now under way and will be the subject of a report to be issued later.

(d) Preparation of the Pulp

Take 10 Whatman ashless tablets and break by hand into a dry 250 ml. beaker. Add 400 ml. water to a Waring blender (Eimer & Amend) and switch on. Add the broken pulp all at once, cover and allow the pulping to continue for 15 seconds. Too long a period of blending results in a slimy pulp which is unsatisfactory. Pour the pulp on a 15 cm. Buchner containing a 15 cm. filter paper. Repeat the pulping process until a box of the tablets has been used (about 300 gms.) and use two Buchners to collect the pulp. Remove the bulk of the water by suction. Transfer the wet pulp to a 4 liter beaker containing 2 liters of boiling 5 per cent HNO_3 and continue the boiling with stirring for 3 minutes. Filter on the two Buchners and wash with 1 liter of water, 1 liter of ethyl alcohol and 2 liters of distilled ether successively, sucking as dry as possible between each addition. Finally, suck as dry as possible, break the pulp by hand, and transfer to a suitable glass container.

(e) Preparation of the Ether

The ether used must be free of peroxides and alcohol. We purchase USP ether in 5 gallon drums. This is allowed to stand in contact with solid KOH pellets for at least 24 hours and is then distilled over solid KOH in an all-glass still. This freshly-distilled ether is used within 1 to 2 days. It can be tested quickly for presence of organic peroxides by means of strong KI solution which is coloured brown by peroxides.

The recovery of the used ether is not considered economical in the laboratory.

The eluent consists of freshly-distilled ether containing 5 per cent HNO_3 v/v. This is prepared just before use and is never kept overnight. The nitric acid used should be kept in a cool place to prevent the formation of oxides of nitrogen and also to minimize the temperature rise when added to the ether.

(f) Preparation of the Glass Column

The columns used are as illustrated in Fig. 1 on page 13. The column is cleaned and dried thoroughly on the hot plate. On cooling, the stopcock is closed and the column is filled with General Electric Dri-Film 9987. This is the run off and the column allowed to stand for 30 minutes. It is then rinsed with water to remove hydrochloric acid. Just before use it is rinsed with a little ether-HNO_3 solution. In order to preserve the water repellant surface the column and wad are removed as soon as elution is complete and the column rinsed with water before setting it aside. A properly prepared column will last for many months if the above procedure is followed.

(g) Separation of Uranyl Nitrate by the Cellulose Column

To the solution in the beaker add prepared cellulose pulp (NOTE d) with stirring plus about twenty drops of ether-nitric solution (NOTE e). Continue adding pulp, about three tablespoonsful in all, while stirring until a slightly damp granular mass is obtained. This is the "wad".

To a previously prepared glass column (NOTE f), add a perforated porcelain plate and then fill column to a depth of six inches with ether-nitric. Add a disc of 41 H Whatman paper and press down on the plate with the glass plunger whose diameter is 2-3 mm. less than the internal diameter of the glass column. Add a little pulp and work the plunger with a moderate up and down motion in the ether-nitric in order to disintegrate the pulp thoroughly. Then open the stopcock wide and allow the ether-nitric to run into a beaker. The pulp will form a small pad above the filter-paper disc and any pulp particles below the disc will be flushed out of the column. Return the contents of the beaker to the column after closing the stopcock. Add more pulp, disintegrate carefully so as not to disturb the pad, allow to settle for a few seconds and then tamp it down with only a very moderate pressure. Repeat this operation with more pulp two or three times until a homogeneous column three inches deep has been formed. About two inches depth of ether-nitric should lie above the top of the column.

Transfer the "wad" to the column with a glass rod and rinse the rod and beaker with ether-nitric. Tamp the wad down on the column

very gently with the plunger and then remove the plunger rinsing it with ether-nitric into the column. Place a 300 ml. Erlenmeyer flask below the column so that the neck of the flask does not contact the outlet tip of the column. See Fig. 1, page 13. Open the stopcock so that the ether runs through at a rate a little less than a continuous stream. Pour about 20 ml. of ether-nitric into the original beaker and, when the ether-nitric level is just above the top of the wad, add this additional ether-nitric from the beaker. Repeat until about 150 ml. of eluent have been collected. Test for complete removal of uranium by catching a drop of the ether eluent on a strip of filter paper. Allow the ether to evaporate and add 1 drop of 0.2 per cent potassium ferrocyanide. Absence of a brown colour shows complete elution of the uranyl nitrate.

The column is removed from its supporting stand and held horizontally. A rubber atomizer bulb is attached to the outlet tip and the wad and column are readily extruded on a glass dish. 0.2 per cent potassium ferrocyanide is now added dropwise from a medicine dropper along the length of the wad and column. The lower boundary of the phase containing iron, etc., is shown by the deep blue colour developed. This boundary should not be more than one quarter of an inch inside the column portion.

To the Erlenmeyer flask add 15-20 ml. of water and distil off the ether on a steam-bath under a hood. With high grade samples a larger volume of eluent is sometimes required. In this event the rate of distillation of the ether should not be too rapid or foaming will occur. The ether vapour is condensed in a water condensor in

series with a 4-liter flask cooled by dry ice. The distillate is discarded by pouring on the ground well away from any buildings or inflammable material. When the distillation appears to be complete, the Erlenmeyer is disconnected from the condenser and allowed to remain on the steam-bath for an additional 5 minutes to remove practically all of the ether.

(h) Precautions in Handling Ether

Since diethyl ether boils at 34.6°C. and the vapour is highly inflammable, particular precautions must be observed by all workers. The ether is received in 5 gallon drums and stored in a special shed attached to the outside north wall of a brick building. Not more than four drums should be kept on hand if this is possible. A single 5 gallon drum is kept in the laboratory where all of the ether work is conducted and as far as possible all of this is done under hoods. No smoking and no open flames or hot plates are permitted in this room. A fire-blanket is mounted outside the laboratory and two CO_2-type fire extinguishers are kept in the other laboratory together with a bucket of sand. The apparatus for distilling the USP ether should be behind a safety-glass shield. Safety goggles and shields are also available. The use of dry ice is very advantageous in condensing ether vapour.

(i) Solution of Solid Samples

It is preferable to use nitric acid alone in the solution of the ore since this shortens the procedure appreciably in the absence of arsenic. If all of the uranium can be dissolved by nitric acid

then the analyst can proceed directly with the column extraction. As previously noted, however, this cannot be done if arsenic is present.

REFERENCES

1. "Modified Mercury Cathode-Cupferron Method for Determination of U_3O_8", Memorandum Series No. 103, Sept. 1949.

2. "The Estimation of Uranium in Low Grade Siliceous Ores by Extraction of Uranyl Nitrate with Ether containing Nitric Acid in the presence of activated cellulose" CRL/AE19

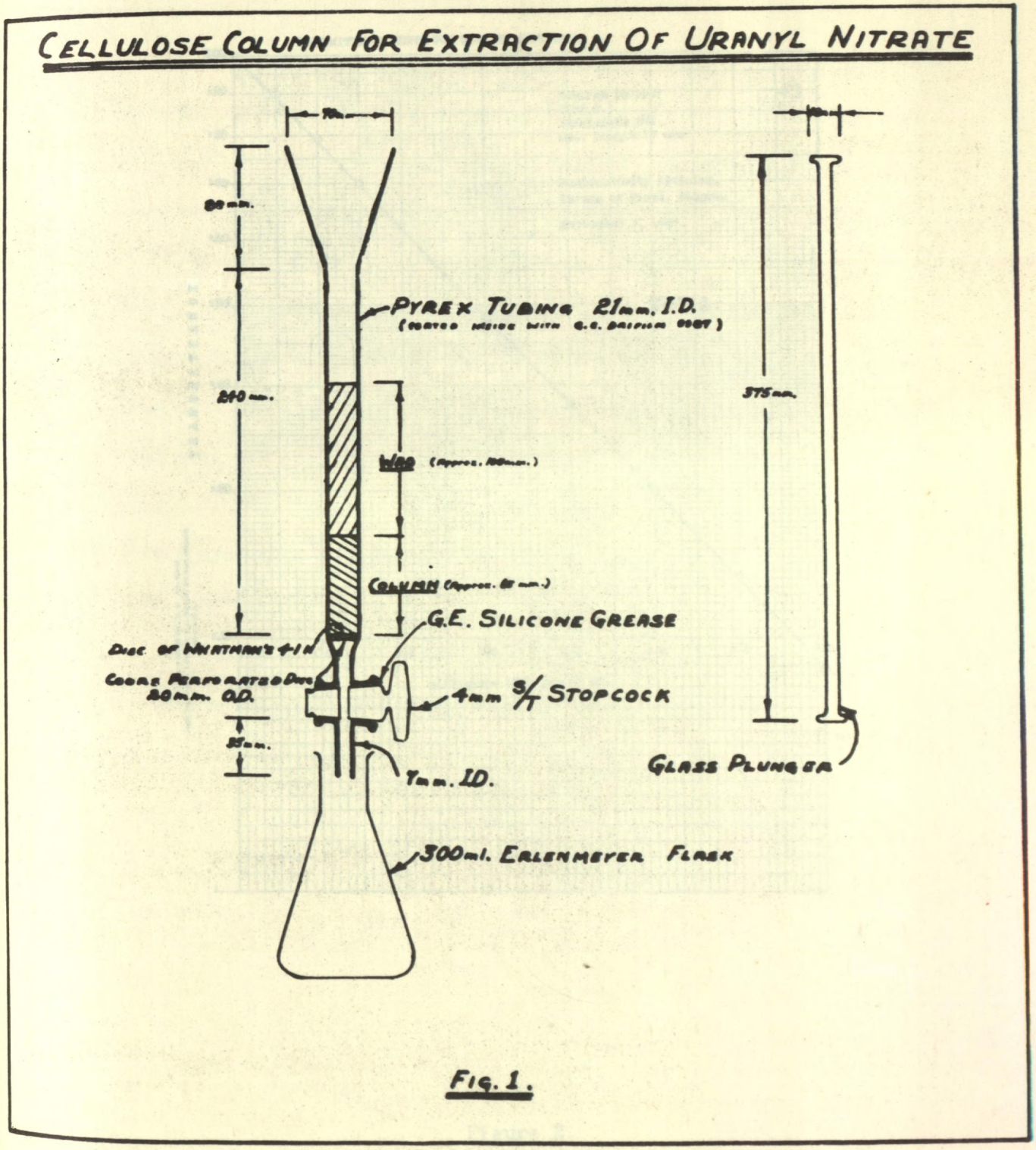


FIG. 1.

Figure 1

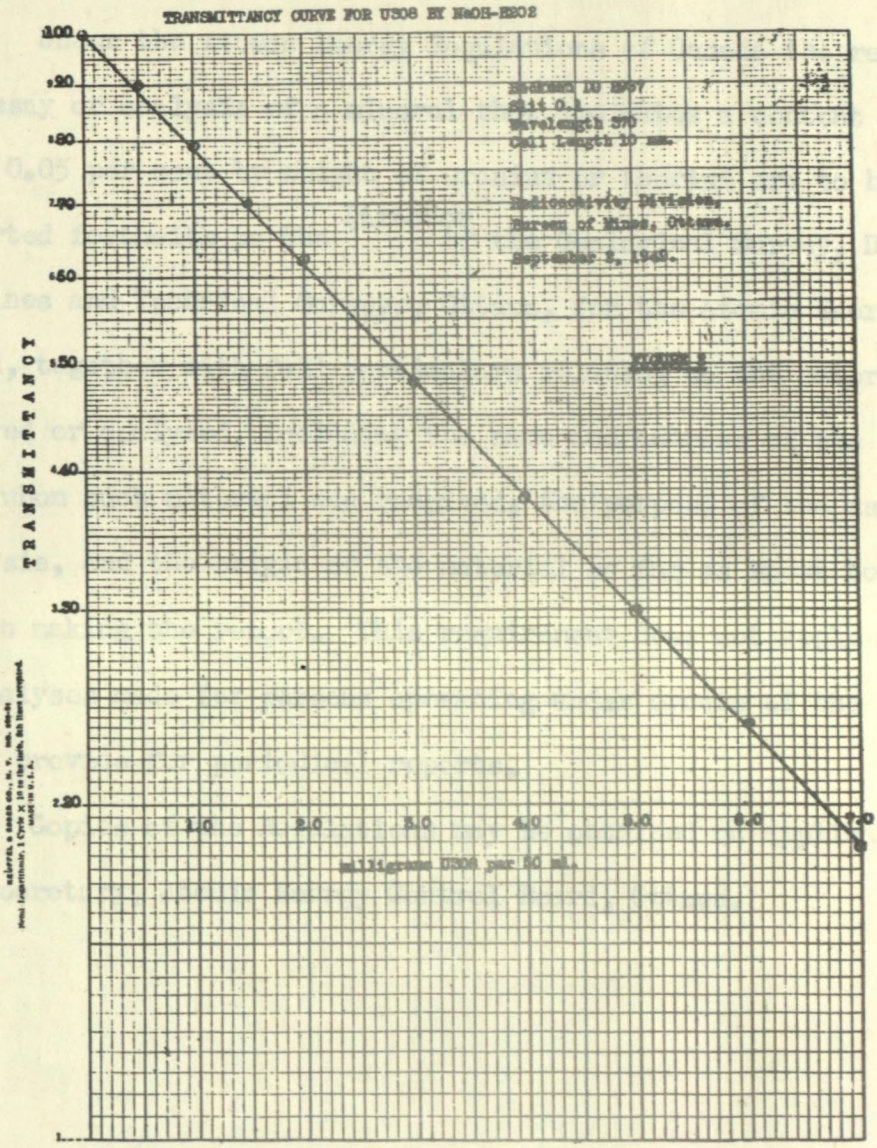

TRANSMITTANCY CURVE FOR UO2 BY NaOH-H2O2
Beckman DU Spy
Slit 0.1
Wavelength 370
Cell Length 10 mm.
Radioactivity Division,
Bureau of Mines, Ottawa.
September 2, 1945.
TRANSMITTANCY
100
90
80
70
60
50
40
30
20
1
1.0
2.0
3.0
4.0
5.0
6.0
7.0
milligrams UO2 per 50 ml.

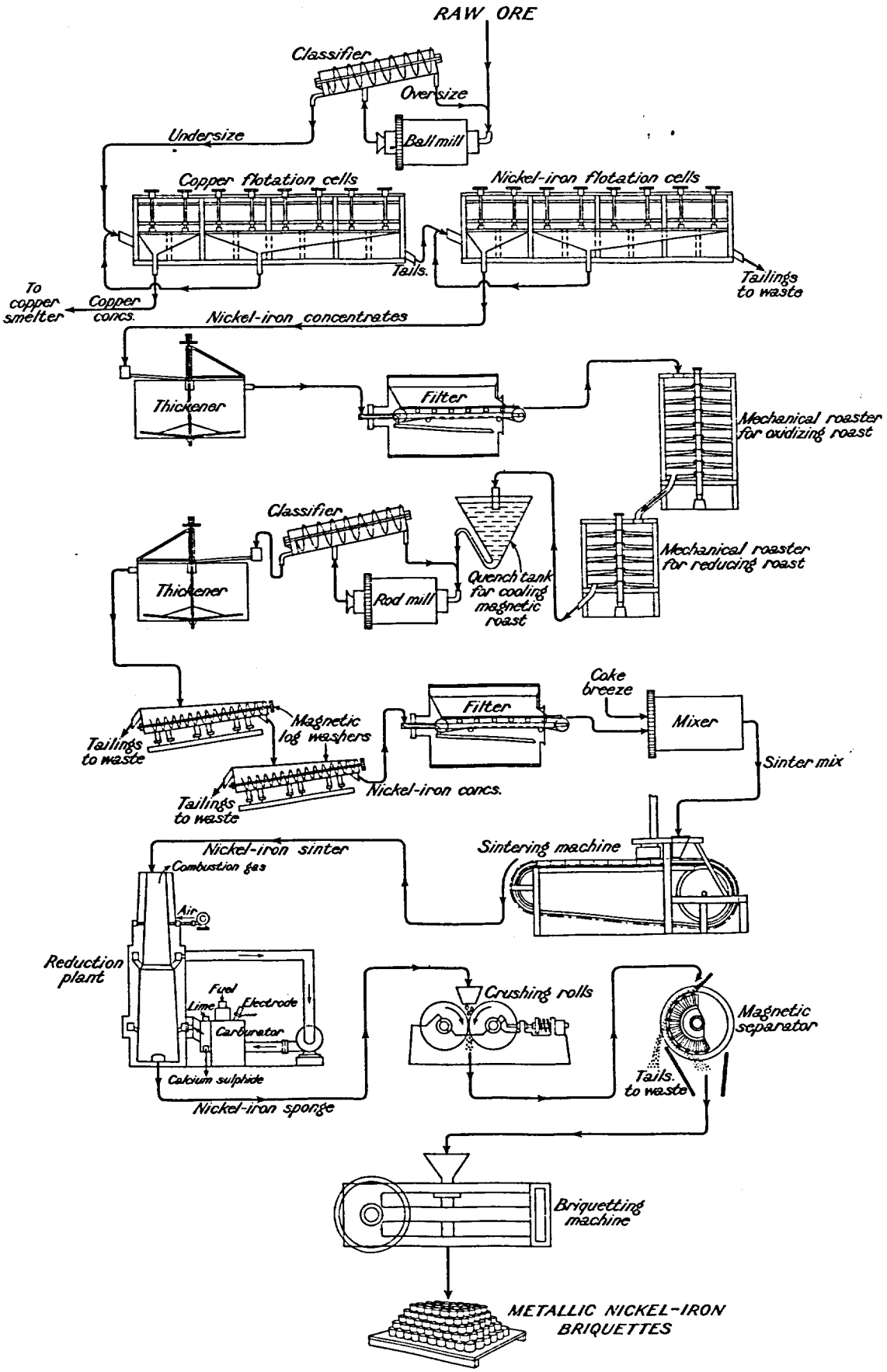
Figure 2

APPENDIX

Reporting of Uranium or Thorium Determinations

Under the Atomic Energy Regulations of Canada the results of an assay or analysis of a mineral that indicates a content of more than 0.05 per cent by weight of uranium or thorium are to be reported forthwith to the Director of the Geological Survey, Department of Mines and Technical Surveys, Ottawa, for the Atomic Energy Control Board, together with full particulars relating to the material assayed or analysed, including the name and address of the person from whom such material was received, the purpose of the assay or analysis, and the origin of the material so far as known to the person making the report. This requirement does not apply to assays or analyses made for persons operating under orders of the Board which provide for periodical reports.

Copies of the Regulations may be obtained on application to the Secretary, Atomic Energy Control Board, Ottawa.



Suggested flow-sheet showing method of producing nickeliferous sponge iron from Sudbury ores.