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THE PRODUCTION OF HEAVY WATER

AT TRAIL, B.C.

by

E. A. Barlow

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## THE PRODUCTION OF HEAVY WATER

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1. INTRODUCTION

The heavy water plant was built as an addition to the Consolidated Mining & Smelting Company's plant at Trail, B.C., to take advantage of the existence of the electrolytic units<sup>1</sup> which provide hydrogen for ammonia synthesis for use in the production of fertilizer. In this respect heavy water must be regarded as a by-product since the major portion of the plant was in existence and operation for many years prior to the commencement of heavy water production. The effect of this is very favorable as regards production cost, as it would be uneconomical to produce D<sub>2</sub>O electrolytically if the hydrogen gas were to be wasted.

The plant may be considered to consist of three parts as follows:

- (a) A primary plant of four stages including the original electrolytic hydrogen plant, plus certain modifications, and the catalytic exchange towers.
- (b) The secondary plant of three stages built especially for heavy water production.
- (c) The control laboratory.

It is understood that the United States government paid the entire cost of the construction of the heavy water plant, including the secondary plant and the necessary modifications to the primary plant. Much of the equipment such as instruments at the catalytic towers, mass spectrometers in the laboratory, etc., bear plates stating that they are the property of the United States government. The additional buildings constructed for the D<sub>2</sub>O plant consist of those required to house the catalytic towers, the secondary plant and the control laboratory.

Power is obtained from the West Kootenay power plants on the Kootenay River, being received at 60,000 volts and stepped down to 830 or 670 volts before it is rectified for use in the electrolytic cells. Ten mercury arc rectifiers are used for this purpose. Approximately 105,000 h.p. is required daily, most of

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1. Smyth, H.D., Atomic Energy for Military Purposes, Sections 9.36 - 9.41

this power being used in the production of hydrogen which amounts to 13,000,000 cubic feet or 36 tons per day<sup>1</sup>.

In the heavy water installations water from the Columbia River is up-graded from 0.0156% by weight of D<sub>2</sub>O to 99.75% plus in the two plants. A production of approximately 1100 lb. of D<sub>2</sub>O a month is obtained.

## 2. PRIMARY PLANT<sup>2</sup>

The primary deuterium oxide plant equipment consists of the original hydrogen installations used in the production of ammonia for the Warfield fertilizer plant plus catalytic exchange towers.

The concentration process is a continuous, counter-current electrolysis and scrubbing operation divided into four stages in which Columbia River water is up-graded in D<sub>2</sub>O content from 0.0156% to 2.25% by weight. The electrolytic equipment consists of 3233 diaphragm type cells divided into 9 batteries of approximately 330 cells each. The first stage is comprised of 7 1/2 batteries or 2729 cells, the second - 378 cells, the third - 96 cells and the fourth stage - 30 cells. In general, the concentration process consists of scrubbing the electrolysed hydrogen gas from the first stage cells with distilled water in the No. 1 catalyst towers in which a selective 3 to 1 preferential pick up of deuterium occurs.

Bottoms from the No. 1 towers constitute the feed of the first stage cells, the hydrogen tops being used for ammonia synthesis. Mixed hydrogen and water vapor, and mixed oxygen and water vapor are drawn off the cells and passed through the hydrogen or oxygen cooler as the case may be. The vapor is condensed and the gases passed on to the No. 1 towers in the case of the hydrogen or to the oxygen scrubber as in the case of the O<sub>2</sub>. The condensate from both coolers is then pumped to an evaporator and distilled to remove all traces of the KOH cell electrolyte. The condensate from the evaporator then becomes the scrubber liquor for the No. 2 tower which scrubs the H<sub>2</sub> gas from the second stage cells and the gaseous product of the No. 3 tower. This process is repeated in all four stages.

The oxygen product of all four stages is piped to a scrubber in which the deuterium content of the entrained vapor is reduced from 0.113% to 0.0156%. The scrubber liquor supplements the feed to the first stage cells. The oxygen by-product is burned in various parts of the Trail smelters.

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1. Cominco - Vol. 8, No. 11.

2. See Figure 1.

Distilled feed water for the hydrogen and oxygen scrubbers and the No. 1 tower is produced by means of two Escher Wyss distillation installations which provide six to seven tons per hour at an approximate cost of 40 cents per ton.

The primary cells, (Fig. 5), called Trail Design Tank type cells, were developed and built by the Consolidated Mining and Smelting Company. Each cell is approximately 4 ft. by 5 ft. by 4 ft. in size and contains 15 plates about 42 in. square which are suspended in an electrolyte of 24 to 25% caustic potash and water. Iron anodes and nickel plated iron cathodes are separated from each other by means of asbestos diaphragms. The hydrogen and oxygen evolved is collected in separate headers built into the steam cured concrete cell covers which have an average life of about four years. Each primary cell draws 10,000 amperes and operates at a 2 volt potential with the exception of 300 cells of the first stage which draw 15,000 amps. each. Current density used is 70 to 75 amperes per square foot. Pressure within the cells is maintained at 3 in. of water pressure and the temperature of the cell is maintained at 70°C. This temperature is varied from time to time to suit operating conditions.

All batteries of cells are connected to nitrogen lines under 7 in. of water pressure, and in case of fire all cells can be flooded with nitrogen from one main valve.

Four Roots Connerville blowers are available for handling the gas from the first stage concentration. Normally three blowers are used, one remaining as a stand-by unit. Second, third, and fourth stage gas is handled by single Roots blowers of smaller size.

Gas from the electrolytic cells of the first stage of the primary concentration is passed through two catalytic towers of identical construction (Fig. 4). Three first stage towers are available but only two are used at any one time. Each column is approximately 140 ft. in height and 8 ft. in diameter, containing 13 double plates spaced 10 ft. apart. Each double plate consists of 2 plates spaced 8 in. apart, each fitted with 358 type V-D-S bubble caps. Twenty scrubbing plates are located in each tower base for the removal of KOH solution entrained from the cells. Located in the 10 ft. space between the double plates, is a steam coil pre-heater and a 4 1/2 in. bed of dry catalyst. The catalyst is granular; individual grains being approximately 1/8" in size. It has been supplied by the United States Government under the designation "Product 43" and is believed to be platinum on a carbon carrier.

Baffles direct the flow down through the catalyst which must be kept dry at all times. Catalyst reactivation is accomplished by passing air at 100°C. through the beds, one reactivation being required per year. Tower temperatures are maintained at 70°C. over

the entire length, the tower of course being completely lagged for heat conservation. The operating pressure at the top is 50 in. of water; pressure drop through the tower is 13 to 14 in. An after heater maintains the tower vapor in a saturated condition at all times, 30,000 to 70,000 lbs. of steam being used for this purpose by each tower.

Second, third and fourth stage towers are of similar design but on a smaller scale. A single tower is used in each of the above stages. The catalyst used is the same in each tower with the exception of the fourth stage installation which uses a material known as Product 80 believed to contain 85% nickel and 15% chromium. This catalyst is not as sensitive to poisoning as the platinum used in the first three stages.

As previously mentioned, in order to prevent the entry of KOH solution to the catalytic towers, condensate from the gas coolers in the first, second and third stages are evaporated and condensed before being pumped to the top of the tower. Periodically still bottoms are blown down to the respective stage from which the KOH was removed.

Condensate from the fourth stage coolers is run to the primary storage tank prior to passing on to the secondary plant.

The following tables constitute typical operating data of the primary plant:

	<u>Electrolyte</u> Wt. % D <sub>2</sub> O	<u>Tower Bottoms</u> Wt. % D <sub>2</sub> O
1st Stage	.098	.044
2nd Stage	.316	.176
3rd Stage	.960	.599
4th Stage	2.25	1.24

	<u>Inlet Gas</u> Wt. % D <sub>2</sub> O	<u>Outlet Gas</u> Wt. % D <sub>2</sub> O
1st Stage Tower	.031	.0056 - .0060 <sup>‡</sup>
2nd Stage Tower	.098	.032
3rd Stage Tower	.302	.108
4th Stage Tower	.689	.323
Oxygen Scrubber	.113	.0156

<sup>‡</sup> .0053 best figure obtained.

Typical tower operating data, third stage tower. (1 tower is sampled each month):

	<u>Wt. % of D<sub>2</sub>O</u>
Tower Feed	.308
Tower Bottoms	.501
Inlet Gas	.302
Sect. 1	.256
Sect. 2	.222
Sect. 7	.137
Sect. 13	.108

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It might also be mentioned here that the overall plant loss per month of D<sub>2</sub>O amounts to approximately 970 lb.

### 3. SECONDARY PLANT<sup>1</sup>

The secondary concentration of deuterium is a three stage, batch operation consisting of 130 cells in stage six, 22 cells in stage seven and 4 cells in stage eight, the cells being arranged in 6 rows of 26 cells each. Originally a fifth stage was used but after the concentration of D<sub>2</sub>O had been built up in the system the fifth stage was found to be unnecessary and the cells in this stage were distributed among the later stages.

The secondary plant receives the 2.25% D<sub>2</sub>O from the primary and up-grades it to 99.75% plus in the three stages used. Each cell in the secondary plant electrolyses approximately 3/4 lb. of water per hour.

The secondary cells (Fig. 6) are cylindrical, being 60 in. high and 18 in. in diameter. They contain a single perforated, cylindrical anode of nickel-plated iron and a water jacketed iron cathode as shown in Fig. 6. A 20 in. cone at the base of the cell allows the electrolyte to be reduced to one-fifth of the original charge without seriously affecting the current density. The cells are maintained at room temperature, cooling being necessary since the fractionation factor of the cell becomes more favourable with decreasing temperature although the cell resistance is adversely affected.

Each cell is operated at 1000 amperes and 2 volts and is charged with 130 lb. of liquid. Twenty-four to twenty-five per cent KOH solution is used as the electrolyte. The electrolysis is carried out until the charge has run down to approximately 20% of the original volume at which time the operation ceases.

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1. See Figure 2

The cells and all connected piping are designed sufficiently strong to withstand a hydrogen - oxygen explosion starting at the operating pressure of 7 in. Hg above atmospheric. (The explosion pressure is said to be 165 p.s.i.).

The hydrogen and oxygen come off the cell mixed and are passed through a KOH dryer to the burner where the  $H_2$ ,  $D_2$  and  $O_2$  are recombined. The gas outlet of the cell also serves as a means of introducing electrolyte.

The burner consists of a gas jet having a gas velocity in excess of the flame propagation velocity.

Since large amounts of heat are necessarily released the burner is water cooled. The product from the burner is returned to an earlier stage or stored as feed for the next cycle of the same stage according to its quality. The sixth and seventh stages require about 145 hr. to run and the eighth stage about 100 hr. Burned gas from the sixth stage is returned to the third stage of the primary plant. The last 7 hr. production of the seventh stage is cycled to the seventh stage feed tank and the first 135 hr. to the sixth stage feed tank. Burned gas from the eighth stage is cycled to the eighth stage feed tank for the last 50 hr. and the first 50 hr. to the seventh stage feed tank.

On completion of the electrolysis the electrolyte is run to a sump where it is treated with  $CO_2$  which converts the KOH to  $K_2CO_3$ . The electrolyte is then pumped to a gas fired evaporator; the condensate from the evaporation then constitutes the feed for the next higher stage. The  $K_2CO_3$  cake remaining in the evaporator is used in the next lower stage electrolyte make up.

The condensate obtained from the eighth stage evaporator is run to the product storage. Heavy water from this tank is then distilled, the pH being corrected before distillation with either  $H_2SO_4$  or  $Na_2O$ , and the refined product run directly into the heavy water shipping drums.

All piping and installations in the secondary plant are of ordinary black iron fabrication with the exception of the eighth stage burner, product storage tank, product still and condenser, which are of stainless steel.

#### 4. CONTROL LABORATORY

The heavy water control is carried out in a separate building near the secondary plant. It is operated by a staff of six men, only one of which is of graduate standing. The laboratory is operated during the day shift only.

A. Isotope Analysis<sup>1</sup>

At an earlier date the measurement of the refractive index as a criterion of isotopic ratio had been tried but was found to be unsatisfactory and therefore abandoned. The methods of analysis now in use are as follows:

- (1) The mass spectrometer
- (2) Density methods
  - (a) Picnometer
  - (b) Westphal balance
  - (c) Falling drop

(1) Mass Spectrometer

Three mass spectrometer units, designed and set up by Dr. Nier, are used for analysis. Two of these are 2-3 tubes and are used at the light water end of the scale, the third is a 3-4 tube used for high purity.

The times used for equilibration of samples are thirty minutes for low grade and one hour for high grade. This allows a high grade analysis to be completed in approximately two hours under ideal conditions.

Samples of intermediate purity are frequently diluted a known amount with light water and then run on the low purity mass spectrometer.

(2) Density Methods

(a) Picnometer

An elaborate type of picnometer is used as a check on the mass spectrograph on high grade samples. The accuracy of this method is  $\pm 0.10\%$ .

In the case of density determinations the sample is invariably distilled. The original sample is of the order of 100 ml. and the first and last 25 ml. of distillate are rejected, the final sample being obtained from the middle 50 ml. cut. A small amount of  $KMnO_4$  is added before distillation to break down any organic material.

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1. Laboratory procedures on isotopic analysis are given in Project 9 C and F Section 951, Report No. 1.

(b) Westphal Balance<sup>1</sup>

All of the intermediate purity range (3 to 98%) is analysed by use of a Westphal balance which is calibrated for distilled water. A 10 c.c. plummet is used. This method is highly regarded, being quick, simple and accurate enough for the purpose. Accuracy is quoted as  $\pm 0.20\%$ .

Separate glassware is kept for each quality range. A dry box is used only for high grade samples.

(c) Falling Drop Method

Although equipment is set up to permit the use of the falling drop method in three purity ranges, it is not favourably regarded. Analysis times are apparently as long as a mass spectrometer determination and it is inherently a secondary method.

B. pH Control

In making pH measurements a locally modified Beckman instrument is used. Three points were stressed as follows:

- (a) The sample must be large and the drum well stirred before sampling.
- (b) The sample must not be stored, but should be used if possible within 15 minutes.
- (c) Far more care must be used than would be expected.

It was noted that pH often altered drastically when a drum of product was stored a few days. The causes of this were not fully known.

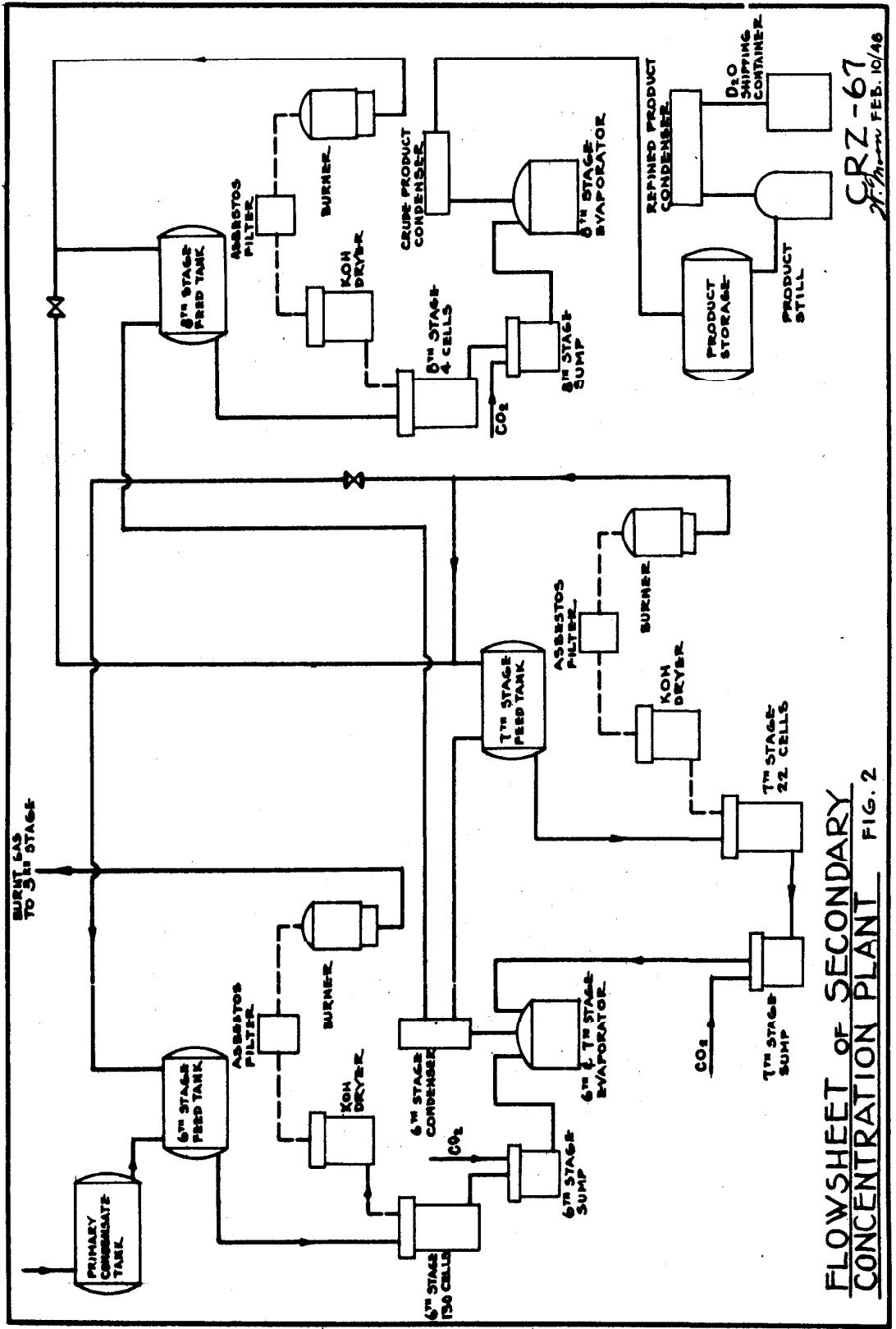
C. Foam Analysis<sup>1</sup>

This method was developed by the Consolidated Mining and Smelting Company Limited as a means of checking the cell electrolyte for foaming tendencies. It consists of a laboratory scale electrolysis of the sample and a means of catching and weighing the foam produced. Analysis is reported as foam number.

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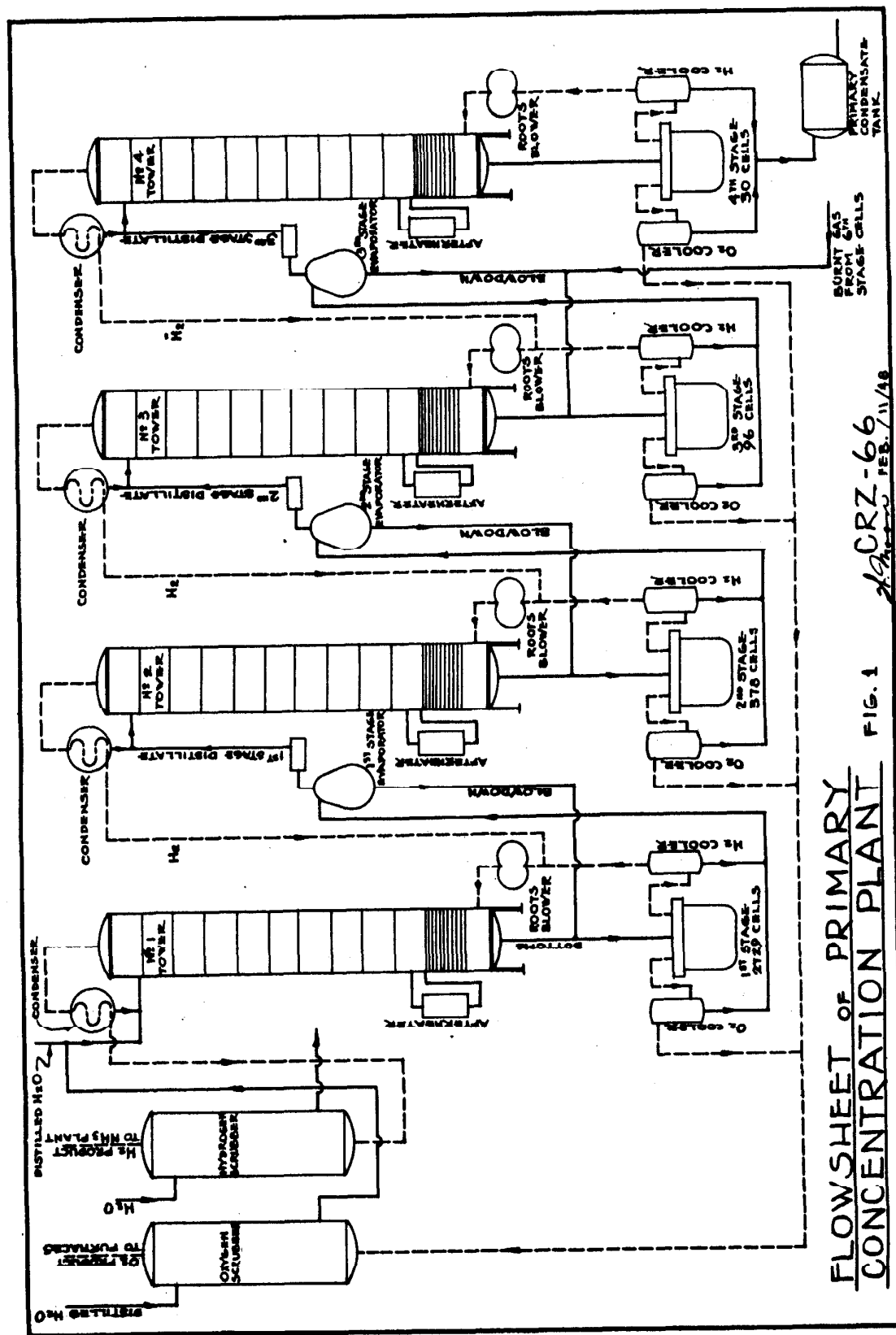
1. See CNF Section 971. Report No. 46 and No. 48.

1. CNF, 199 Report No. 6.



FLOWSHEET OF SECONDARY  
 CONCENTRATION PLANT FIG. 2

CRZ-67  
 J. H. Moore FEB. 10/46

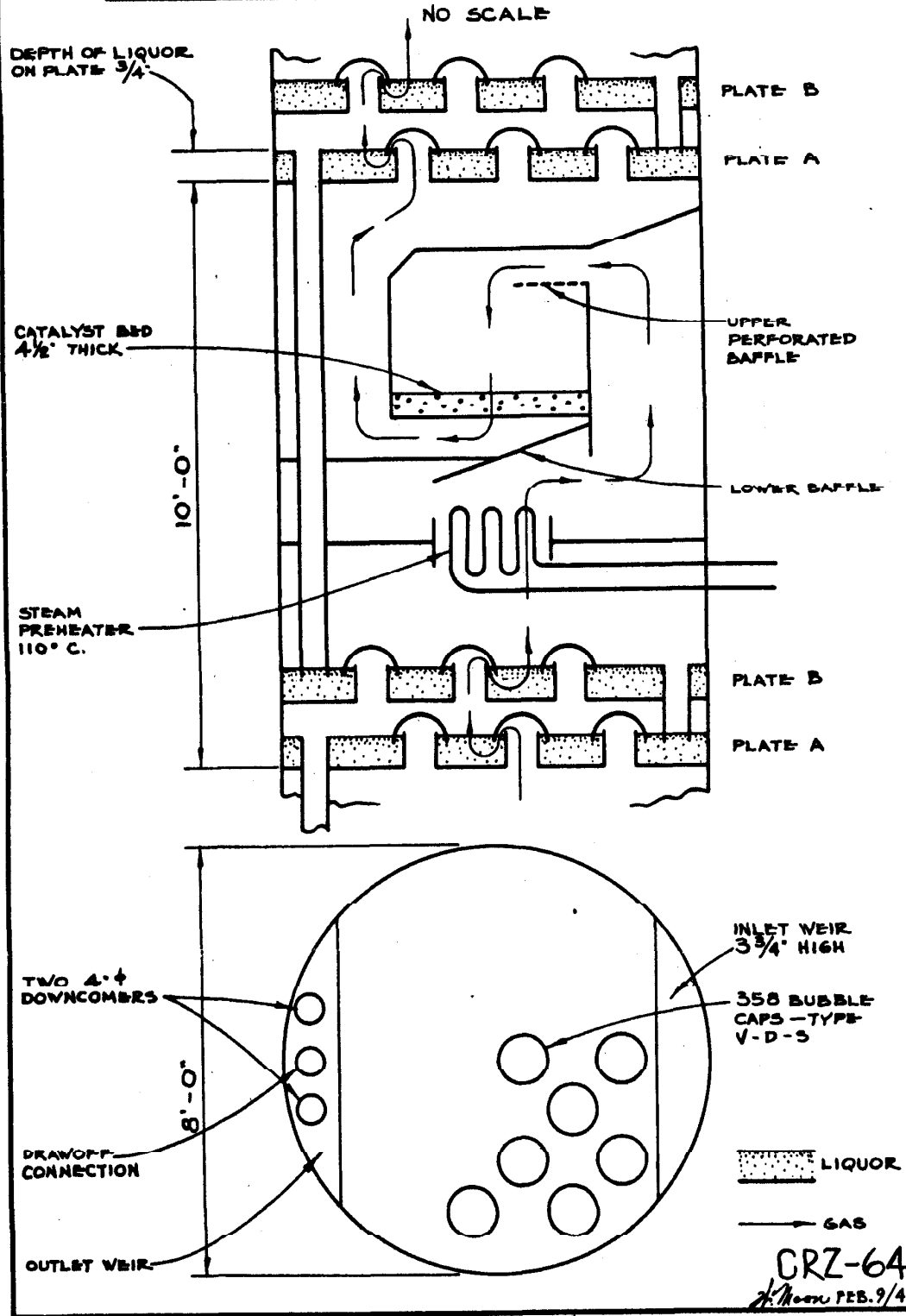


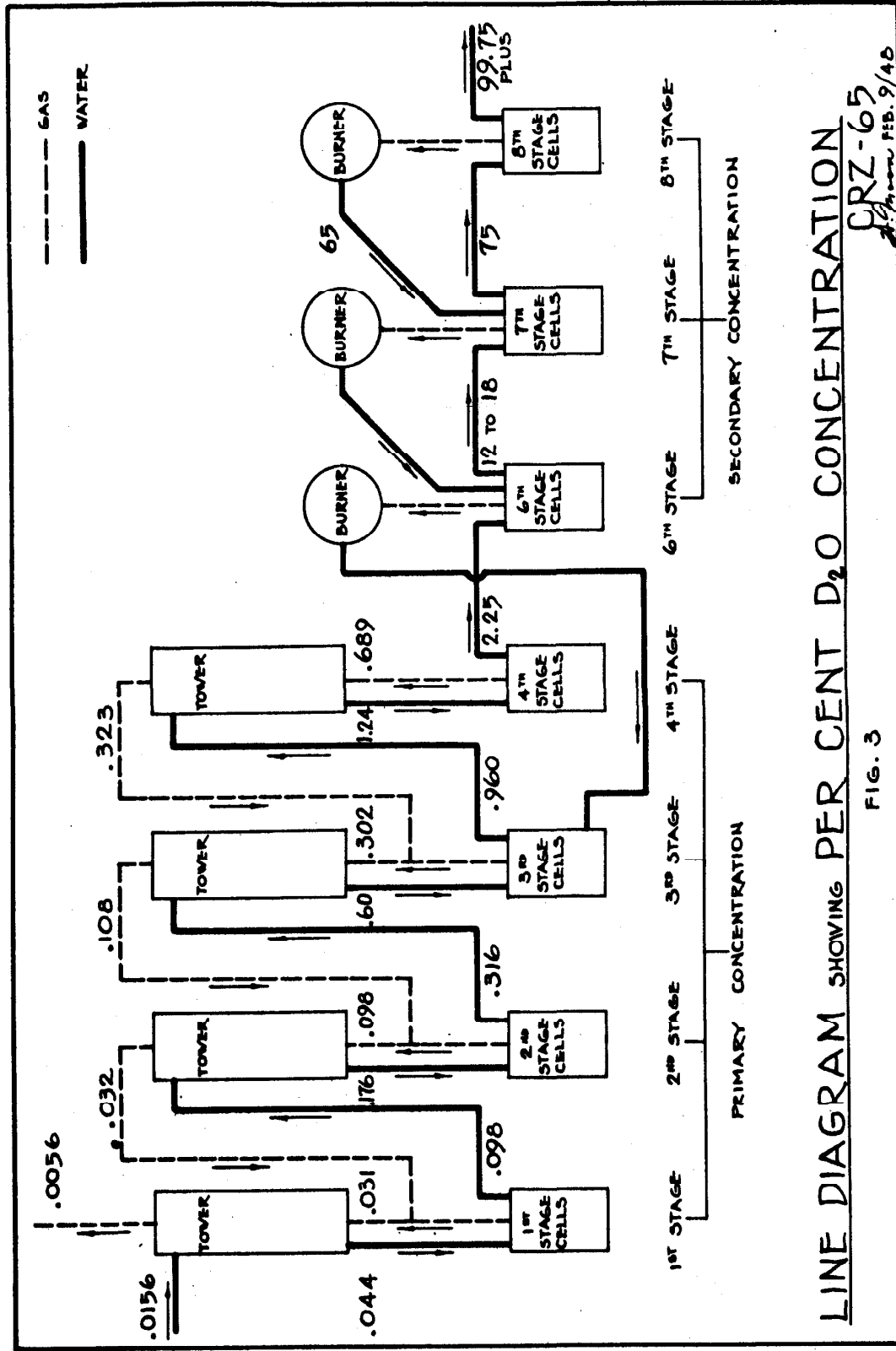
FLWSHEET OF PRIMARY  
CONCENTRATION PLANT FIG. 1

APCRZ-66  
FEB. 7 11/48

# SECTION OF PRIMARY TOWER

FIG. 4



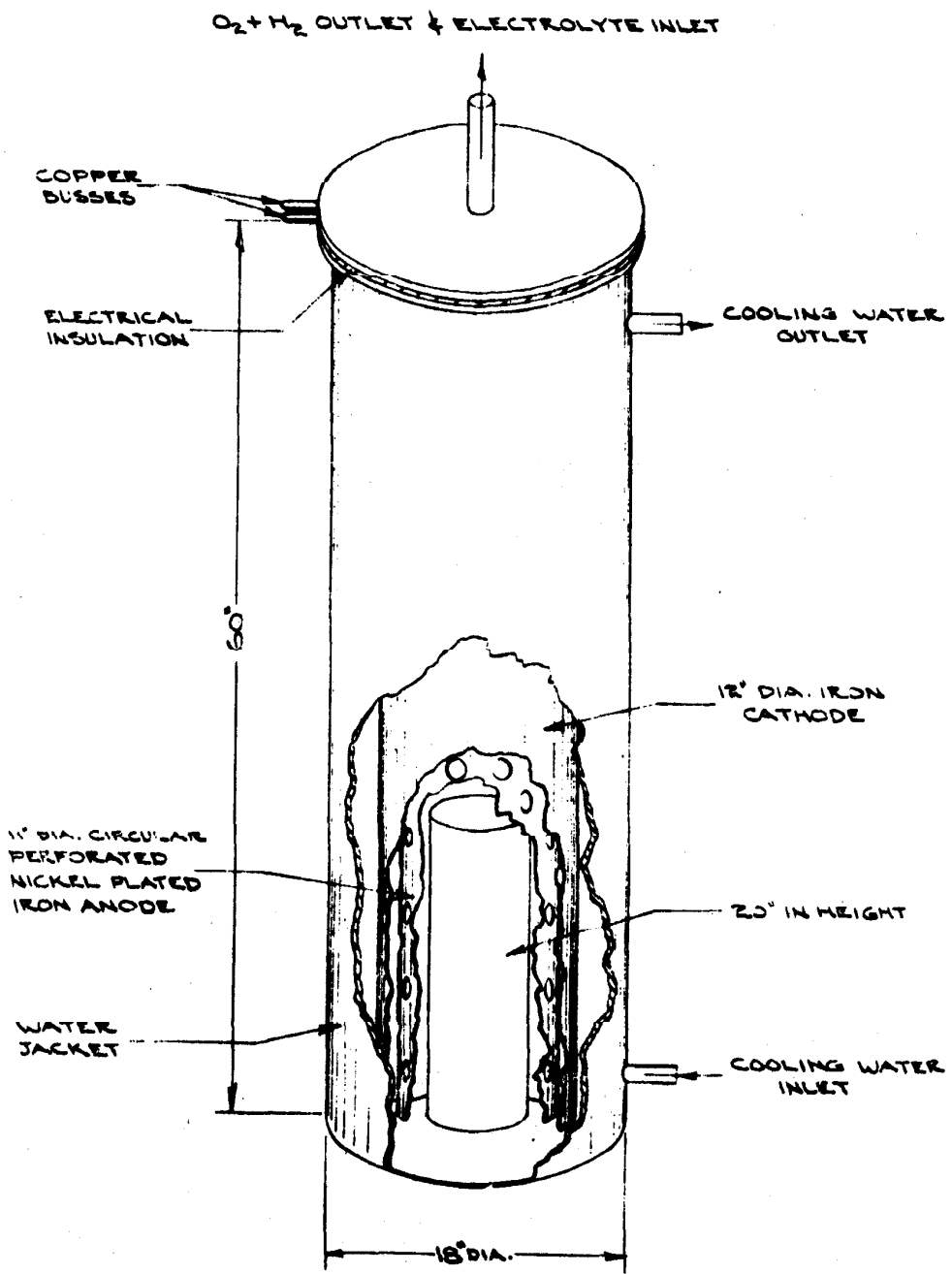


LINE DIAGRAM SHOWING PER CENT D<sub>2</sub>O CONCENTRATION

CRZ-65  
 FEB. 9/40

FIG. 3

CRZ-73



SECONDARY HYDROGEN CELL

FIG. 6.

CRZ 72

