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SUMMARY REPORT

ON

TASK ORDER NO. C
(Phase III)

EB-139D
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August 31, 1959

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April 20, 1960

Dear Sir:

Enclosed is the "Summary Report on Task Order No. C (Phase III)", which describes the research performed under this Task Order during the period January 1 through August 31, 1959.

The prototype full-scale generator unit, with accessories, and also the experimental 1/5-scale generator are available for shipment. If you will provide an appropriate address, we shall be glad to transmit these units to you.

We have enjoyed working on this development and feel that the resulting prototype generator provides an effective unit for generating the required amount of hydrogen under the specialized service conditions. If you should be interested in discussing any further refinements in the design or any other aspects of this unit, or possibly other special types of hydrogen-generation equipment, please do not hesitate to call on us.

We would appreciate any comments which you or your associates might care to make with regard to the research.

Sincerely,

[redacted] 50X1

ABW:mes

In triplicate

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SUMMARY REPORT

ON

TASK ORDER NO. C

(PHASE III)

August 31, 1959

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SUMMARY REPORT

ON

TASK ORDER NO. C

(PHASE III)

August 31, 1959

INTRODUCTION

This report summarizes the research carried out under Task Order No. C, during the period January 1 through August 31, 1959.

The over-all objective under Task Order No. C was to design and develop a prototype generator which would be capable of producing approximately 3,500 cu ft of hydrogen, at an isolated site, in a period of 60 min or less, and, at the same time, would satisfy other specified operational requirements and conditions. The "Summary Report on Task Order No. C (Phase II)" dated December 31, 1958, which summarized the results of the Phase II study, described the underlying research, design, and method of operation of the prototype generator at temperatures between 50 and 90 F. It was concluded in the Phase II study that to provide for the operation of the generator at temperatures between approximately 50 and 32 F would require additional investigation. Described herein are the results of the research carried out in relation to the cold-weather operation of the prototype generator.

SUMMARY AND CONCLUSIONS

The entire research program performed under Task Order No. C has established the requirements for generating 3,500 cu ft of hydrogen in less than 60 min under field conditions where natural water may vary in temperature between 32 and 90 F. For temperatures between 54 and 90 F, a 560-gal pool of water containing 100 lb of sodium borohydride is required. Five gallons of catalyst solution, consisting of 6 to 37 lb of cobaltous chloride hexahydrate dissolved in water, is added; the amount of cobaltous chloride hexahydrate used depends on the initial pool temperature and is selected from a prescribed chart listing the weight of catalyst for various initial temperatures. For temperatures of 32 to 54 F, the generation is carried out with a pool containing 100 lb of sodium borohydride in 250 gal of water. The catalyst requirement in this temperature range varies between 8.2 and 28 lb.

A full-scale test was performed with the prototype generator resting on dry land and using water at a temperature of 36 F; this was completed successfully in 15 min. The hydrogen generated was collected in a balloon and had a measured lift of 223 lb (exclusive of the weight of the balloon and valving).

STATEMENT OF THE PROBLEM

The prototype generator developed and demonstrated in the Phase II study used 560 gal of water and 100 lb of sodium borohydride. The amount of cobaltous chloride hexahydrate catalyst required to achieve a total generation time of about 40 min for temperatures between about 50 and 90 F varied between 46 and 6 lb, respectively.

On extrapolation of these data to near-freezing conditions, it became apparent that excessively large quantities of catalyst would be required. At 36 F, for example, 100 lb of catalyst would be needed for generation in approximately 40 min. It was not feasible to attempt to use such a large quantity of catalyst because:

(1) It exceeded the reported solubility of $CoCl_2 \cdot 6H_2O$ in 5 gal of solution at 36 F

(2) It represented too much of a load for one man to handle conveniently

(3) It was expected to consume a measurable quantity of sodium borohydride and, in the process, would release a large quantity of hydrogen too rapidly at the start of the generation.

Therefore, in an attempt to provide for practical generation under cold-weather operating conditions, it appeared prudent to set 5 gal of saturated catalyst solution as a maximum amount of solution which could be used for full-scale generation. This meant that, for example, at about 32 F, no more than 35 lb* of cobaltous chloride hexahydrate could be used.

The experimental program was subsequently directed toward suitably generating hydrogen in a period of 60 min or less using no more than 35 lb of catalyst.

MATERIALS, EQUIPMENT, AND PROCEDURES FOR HYDROGEN GENERATION

Described below are the materials and equipment, and the operating procedures for generating approximately 3,500 cu ft of hydrogen in the Task Order No. C generator under specified conditions at an isolated site, at which there would be only a pool of surface water sufficiently large to float the generator, and at ambient temperatures ranging from about 32 to 90 F. Under service conditions, depending on the ambient temperature, the operator would have to decide whether the generation would be effected from a 560-gal or a 250-gal system.

To facilitate a comparison of the two systems and as a matter of general convenience, the materials, equipment, and recommended operating procedures for both systems are described below; those for the 560-gal system, for operation at temperatures

* During the early stages of the Phase III study, the maximum solubility of cobaltous chloride in 5 gal of saturated solution at low temperatures was taken as 40 lb, based on data in the literature. When it was subsequently realized that the appropriate value was approximately 35 lb, the experiments were redesigned accordingly.

ranging from 54 to 90 F, had been included previously in the "Summary Report on Task Order No. C (Phase II)" dated December 31, 1958, and as presented below, reflect modifications based on the research performed in the Phase III study. The procedure for the 560-gal system is described for application with the generator floating on a pool of water, while that for the 250-gal system is presented for the generator set up on dry land. However, with only a few modifications of either procedure, the generator could be operated as a 560-gal system on dry land, or as a 250-gal system floating on a pool. The items of materials and equipment are generally presented below in the sequence in which they would be needed in order to carry out the generating procedure.

Materials List for Operation at 54 to 90 F With Floating Generator

For Generation of Hydrogen

(1) Hydrogen generator

(2) Air pump, capacity about 70 cu.in. per stroke

(3) Fabric bag for weights, with drawstring, about 300-cu.-in. capacity

(4) Weights, 15 lb, as rocks or sand, probably available at site

(5) Rope, 1/4 in., about 40-ft length

(6) Tools: knife, pliers, dipper, and funnel

(7) Adhesive tape

(8) Solution container, 5-gal plastic wide-mouth bottle with stopper

(9) Sodium hydroxide, 2 lb, in moisture-proof, unbreakable, nonmetallic package

(10) Rubber gloves, shoulder length

(11) Sodium borohydride, 100 lb of crystals in five 20-lb moisture-proof, unbreakable, nonmetallic packages

(12) Thermometer, all-metal dial type, 32 to 120 F in 1 F increments

(13) Chart showing weight of catalyst required at various initial temperatures of sodium borohydride solution

(14) Cobaltous chloride hexahydrate catalyst, 46 lb of crystals; in individual moisture-proof, unbreakable, nonmetallic packages, 3 of 10 lb each, 2 of 5 lb each, 5 of 1 lb each, and 2 of 1/2 lb each.

<u>For Collection of Hydrogen</u>

(1) Balloon (including gas-inlet tube)

(2) Tarpaulin

(3) Sand bags

(4) Ropes

(5) Relief-valve and balloon-connector assembly.

Recommended Procedure for Operation at 54 to 90 F With Floating Generator

(1) Select a site for operation that provides a water-pool depth of about 4 ft near the bank.

(2) Unpack the hydrogen generator close to the water edge. Unfold the generator pack in a position to favor easy inflation, with the air valve accessible.

(3) Attach the air pump to the air valve. Inflate the air chamber (with about 700 strokes of the pump) until the generator stands firmly on its supporting stays.

(4) Detach the air pump and close the air valve.

(5) Select about 15 lb of rocks or sand at the site. Place in the fabric weight bag and tie the mouth of the bag. The proper weight of rocks may be estimated by comparison with an equal weight of packaged catalyst crystals.

(6) Tip the generator and tie the weight bag to the center of the bottom with the straps provided.

(7) Attach a rope to the generator loop so that the floating generator does not drift. Anchor the other end of the rope on shore.

(8) Slide the generator into the water, and push it away from the bank until it floats freely.

(9) Push both of the water-inlet tubes into the generator and lay them along the inside of the generator wall.

(10) Tilt and resettle the generator in the water several times to dislodge any air bubbles trapped under the bottom of the generator. Make certain that the weight bag is hanging free from the bottom. Recheck the position of the water-inlet tubes along the inside wall of the generator as necessary during the filling period of about 55 min.

(11) While the water is running into the generator, spread the tarpaulin on the ground, unpack the balloon, and lay it out on the tarpaulin; be careful to avoid damage to the balloon fabric. Prepare the balloon auxiliary equipment for use during balloon inflation. Attach the T-shaped relief-valve and balloon-connector assembly to the balloon inlet tube by slipping the free end of the inlet tube over the open end of the connector assembly corresponding to the bottom of the T. Wrap adhesive tape in and around the end of the inlet tube so as to attach the inlet tube firmly to the connector assembly with a joint which will not leak gas.

(12) After the generator has filled to the proper level, with the bottom fully extended by the attached weight, pull out both of the water-inlet tubes and knot each to shut off the water inlets.

(13) Put on the rubber gloves.

(14) Open the 2-lb package of sodium hydroxide flakes and pour them into about 1 gal of water in the 5-gal plastic container. Shake briefly to dissolve, and pour the solution slowly through the open gas exit into the generator pool. Induce some mixing by tipping the generator a few times.

(15) Add the sodium borohydride crystals to the generator pool by opening and emptying one package at a time into the open gas exit.

(16) Check the pool for undissolved borohydride crystals by dipping out a small sample from the center bottom and inspecting. Stir with the dipper or tilt the generator to speed up the mixing and solution, if necessary.

(17) Measure the temperature of the solution by inserting the thermometer into the generator through the open gas exit.

(18) Determine the weight of the catalyst required by referring to the chart (Table 1).

(19) Make up the catalyst solution in the 5-gal plastic container. First, fill the container about one-third full of water, add some of the catalyst, and shake to dissolve. Add more water (corresponding to about one third the volume of the 5-gal container)

TABLE 1. AMOUNT OF CATALYST REQUIRED FOR HYDROGEN GENERATION AT TEMPERATURES BETWEEN 54 AND 90 F

Weight of Sodium Borohydride: 100 lb
Weight of Sodium Hydroxide: 2 lb
Volume of Catalyst Solution: 5 gal
(made up on basis of values given below)
Volume of Generator Solution: 560 gal
Generation Time: Approximately 40 min

Initial Temperature of Solution, F	Weight of Catalyst, lb
90	6
88	6.5
85	7.5
82	8.5
80	9.5
78	10.5
76	11.5
74	13
72	14.5
70	16
68	17.5
66	19.5
64	21.5
62	24
60	27
58	30
56	33.5
54	37

and the remaining catalyst, and shake again. Fill the container to the top with more water. Insert the container stopper, and shake or roll the container to mix the solution. Set the container (with the solution) upright near the generator at the water edge.

(20) Attach the balloon to the gas exit of the generator by inserting the open end of the relief-valve and balloon-connector assembly into the gas-exit tube, and taping it in position with adhesive tape so that the joint will be reliable and will not leak gas. Arrange the balloon inlet tube so that the balloon will start to fill without attention while the catalyst solution is being added to generator.

(21) Support the full container of catalyst solution upright on the top edge of the floating generator, remove the stopper, and pull the open end of the filling funnel over the neck of the container and down around the body of the container.

(22) Tip the container and pour the catalyst solution through the funnel into the catalyst reservoir on the top of the generator.

(23) Hydrogen generation will start as soon as the catalyst solution starts to run into the generator pool from the reservoir. Quickly tie off the

flexible spout of the filling funnel to prevent any loss of hydrogen.

(24) Attend the balloon during the filling operation. No further control of hydrogen generation is needed.

Materials List for Operation at 32 to 54 F on Dry Land

For Generation of Hydrogen

(1) Hydrogen generator

(2) Air pump, capacity about 70 cu. in. per stroke

(3) Tools: Knife, pliers, dipper, funnel, and 2-gal (nominal) plastic or rubber bucket

(4) Adhesive tape

(5) Solution container, 5-gal plastic wide-mouth bottle with stopper

(6) Sodium hydroxide, 0.9 lb, in moisture-proof, unbreakable, nonmetallic package

(7) Rubber gloves, shoulder length

(8) Sodium borohydride, 100 lb of crystals in five 20-lb moisture-proof, unbreakable, nonmetallic packages

(9) Thermometer, all-metal dial type, 32 to 120 F in 1 F increments

(10) Chart showing weight of catalyst required at various initial temperatures of sodium borohydride solution

(11) Cobaltous chloride hexahydrate catalyst, 28 lb of crystals; in individual moisture-proof, unbreakable, nonmetallic packages, 1 of 10 lb, 2 of 5 lb each, 7 of 1 lb each, and 5 of 0.2 lb each.

For Collection of Hydrogen

(1) Balloon (including gas-inlet tube)

(2) Tarpaulin

(3) Sand bags

(4) Ropes

(5) Relief-valve and balloon-connector assembly.

Recommended Procedure for Operation at 32 to 54 F on Dry Land

(1) Select a site for operation that provides a relatively flat area, about 9 to 11 ft in diameter, as close as possible to the source of water.

(2) Unpack the hydrogen generator on the flat area as close as possible to the source of water. Unfold the generator pack in a position to favor easy inflation, with the air valve accessible.

(3) Attach the air pump to the air valve. Inflate the air chamber (with about 700 strokes of the pump)

until the generator stands firmly on its supporting stays.

(4) Detach the air pump and close the air valve.

(5) Knot each of the water-inlet tubes at the bottom of the generator so as to close them off.

(6) Using the 2-gal (nominal) bucket, pour 250 gal of water into the generator through the open gas-exit tube. This involves adding 125 bucketfuls of water. (In the generator, 250 gal of water represents a pool with a depth of 8.2 in. If necessary, the operator can coarsely check the depth of the water in the generator by using a "dip stick" method, that is, by inserting a tree branch, or its equivalent, in the vertical position through the generator gas exit and estimating the length of the branch wetted by the water. If there is any doubt in the operator's mind as to whether he has added enough water, it would be safest if he poured in more.) The filling operation can be done in about 15 to 20 min.

(7) Spread the tarpaulin on the ground, unpack the balloon, and lay it out on the tarpaulin; be careful to avoid damage to the balloon fabric. Prepare the balloon auxiliary equipment for use during balloon inflation. Attach the T-shaped relief-valve and balloon-connector assembly to the balloon inlet tube by slipping the free end of the inlet tube over the

open end of the connector assembly corresponding to the bottom end of the T. Wrap adhesive tape in and around the end of the inlet tube so as to attach the inlet tube firmly to the connector assembly with a joint which will not leak gas.

(8) Put on the rubber gloves.

(9) Open the 0.9-lb package of sodium hydroxide flakes and pour them into about 1 gal of water in the 5-gal plastic container. Shake briefly to dissolve, and pour the solution slowly through the open gas exit into the generator pool. Induce some mixing by tipping the generator a few times.

(10) Add the sodium borohydride crystals to the generator pool by opening and emptying one package at a time into the open gas exit.

(11) Check the pool for undissolved crystals by dipping out a small sample from the center bottom and inspecting. Stir with the dipper or tilt the generator to speed up the mixing and solution, if necessary.

(12) Measure the temperature of the solution by inserting the thermometer into the generator through the open gas exit.

(13) Determine the weight of the catalyst required by referring to the chart (Table 2).

TABLE 2. AMOUNT OF CATALYST REQUIRED FOR HYDROGEN GENERATION AT TEMPERATURES BETWEEN 32 AND 54 F

Weight of Sodium Borohydride: 100 lb
Weight of Sodium Hydroxide: 0.9 lb
Volume of Catalyst Solution: 5 gal
(made up on basis of values given below)
Volume of Generator Solution: 250 gal
Generation Time: Approximately 20 min

Initial Temperature of Solution, F	Weight of Catalyst, lb
54	8.2
52	9.2
50	10.2
48	11.6
46	12.8
44	14.0
42	16.0
40	17.6
38	20.0
36	22.4
34	24.8
32	28.0

(14) Make up the catalyst solution in the 5-gal plastic container. First, fill the container about one-third full of water, add some of the catalyst, and shake to dissolve. Add more water (corresponding to about one third the volume of the 5-gal container) and the remaining catalyst, and shake again. Fill the container to the top with more water. Insert the container stopper, and shake or roll the container to mix the solution. Set the container (with the solution) upright near the generator.

(15) Attach the balloon to the gas exit of the generator by inserting the open end of the relief-valve and balloon-connector assembly into the gas-exit tube, and taping it in position with adhesive tape so that the joint will be reliable and will not leak gas. Arrange the balloon inlet tube so that the balloon will start to fill without attention while the catalyst solution is being added to generator.

(16) Support the full container of catalyst solution upright on the top edge of the generator, remove the stopper, and pull the open end of the filling funnel over the neck of the container and down around the body of the container.

(17) Tip the container and pour the catalyst solution through the funnel into the catalyst reservoir on the top of the generator.

(18) Hydrogen generation will start as soon as the catalyst solution starts to run into the generator pool from the reservoir. Quickly tie off the flexible spout of the filling funnel to prevent any loss of hydrogen.

(19) Attend the balloon during the filling operation. No further control of hydrogen generation is needed.

CHEMICAL ACTIVITY

Experimental Work

Studies were carried out in the 1/5- and full-scale generators designed and prepared under the Phase II program. All of the generation experiments were performed on dry land; this was in contrast to portions of the Phase II program in which the full-scale and some of the other tests had been run with the generators floating on a body of water. Complete descriptions of the two generators and methods of operation were presented in the "Summary Report on Task Order No. C (Phase II)" dated December 31, 1958.

Results

In order to attain the goals of the Phase III study, the experimental program was divided into two parts. The first part was concerned with determining the lowest temperature at which generation could be completed in 60 min (maximum) using 5 gal of saturated catalyst solution (approximately 35 lb of catalyst). The second part involved establishing a new catalyst-temperature relationship for a more concentrated sodium borohydride solution, for use in generation between the "lowest temperature", as determined in the above-mentioned Part 1 of the program, and 32 F.

Part 1: Low-Temperature Limit for Generation Under "Standard" Conditions

Runs 3, 8, 9, 10, 11, and 12, listed in Table 3, are 1/10-scale tests from which the low-temperature limit of operation under "standard" conditions (100 lb of sodium borohydride in 560 gal of water) was obtained. Figure 1 presents a plot of some of these data; it indicates that, under "standard" conditions, the prototype generator can be used to produce hydrogen in 60 min or less at a minimum temperature of approximately 53 F when a maximum of 35 lb of catalyst is involved. It is to be noted, in Figure 1, that the catalyst-temperature line based on the Phase II study intersects the extrapolated line for the data of Runs 10, 11, and 12 and the 35-lb catalyst line at approximately 53 F.

TABLE 3. RESULTS OF HYDROGEN-GENERATION TESTS TO ESTABLISH MINIMUM TEMPERATURE FOR OPERATION UNDER "STANDARD"* CONDITIONS

Run No.	Reaction Solution: Scale	Reaction Solution: $NaBH_4$, lb	Reaction Solution: Water, gal	Reaction Solution: Depth, in.	Temperature, F: Initial	Temperature, F: Rise	Catalyst: Am't, lb	Catalyst: Vol of Solution, gal	Total Generation Time, min
3	1/10	10.0	56	9	39	57	4.0	1.0	51
8	1/10	10.0	56	9	33	58	4.0	1.0	74
9	1/10	10.0	56	9	34	58	4.0	1.0	84
10	1/10	10.0	56	9	37	60	3.0	0.5	112
11	1/10	10.0	56	9	42	59	3.2	0.5	91
12	1/10	10.0	56	9	46	59	3.3	0.5	77

* Under full-scale conditions, 560 gal of water and 100 lb of sodium borohydride.

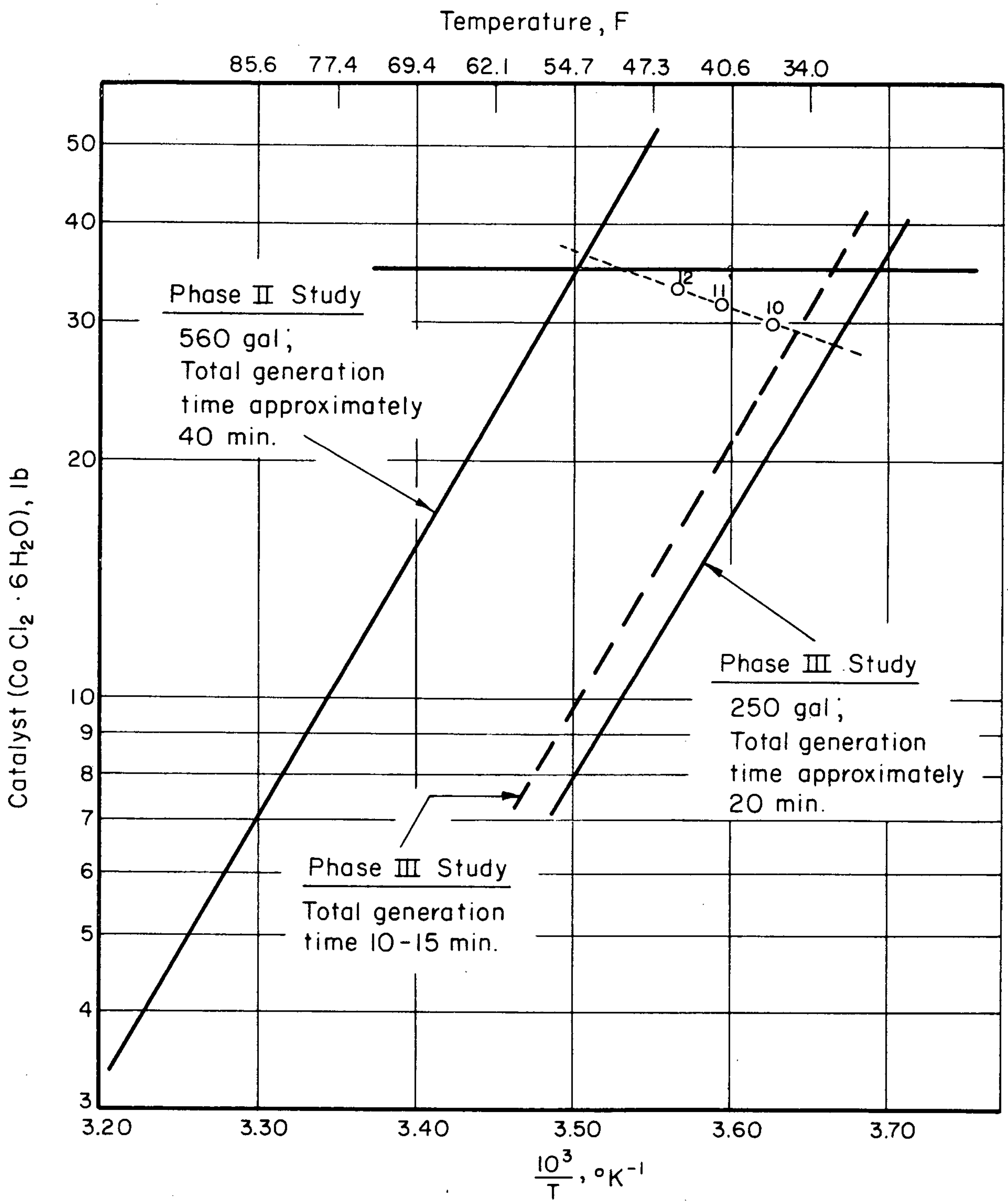

FIGURE 1. CATALYST REQUIREMENT FOR LARGE-SCALE GENERATION OF HYDROGEN

Runs 1, 2, 4, 5, 6, and 7, shown in Table 4, were small, bench-scale experiments which were performed in a 10-1/2-in.-diameter glass reactor. These small-scale tests were run to explore the effect of catalyst distribution, depth of reactor pool, and mixing characteristics on total generation time; and involved the same relative borohydride concentration as the previously mentioned 1/10-scale tests.

Part 2: A Catalyst-Temperature Relationship for Full-Scale Generation With 250 Gal of Water

After approximately 53 F was determined as the low-temperature limit for suitable generation using 560 gal of water, it was then necessary to establish the proper conditions for generating hydrogen at temperatures between 53 and 32 F. Information obtained in the Phase I study had indicated that this would be achieved most readily by increasing the concentration of sodium borohydride. This change would result in less water being used in preparing the generator solution; consequently, the temperature rise and the average temperature in the system would be greater, and the rate of generation could be increased without using more than 35 lb of catalyst.

Runs 14 through 17, listed in Table 5, were the 1/10- and 1/5-scale experiments from which a catalyst-temperature relationship was obtained for full-scale generation using 250 gal of water. Run 13 was a 1/10-scale test based on a 400-gallon

TABLE 4. RESULTS OF SMALL-SCALE EXPLORATORY GENERATION TESTS

Run No.	Reaction Solution			Temperature, F		Catalyst			Total Generation Time, min	Remarks
	$NaBH_4$, lb*	Water, liter*	Depth, in.	Initial	Rise	Am't, g	Vol of Solution, cc	Addition Site		
1	0.12	2.5	1-3/4	64	34	2.97	50	Pool center	42	-
2	0.12	2.5	1-3/4	66	36	2.97	50	Over entire pool surface	50	-
4	0.35	7.5	5-1/2	68	50	8.92	150	Pool center	42	-
5	0.35	7.5	5-1/2	64	48	8.92	150	Over entire pool surface	51	-
6	0.35	7.5	5-1/2	70	50	8.92	150	Pool center	40	-
7	0.35	7.5	5-1/2	71	51	8.92	150	Over entire pool surface	25	Solution stirred for 30 sec after catalyst addition

Note: These tests were conducted in a 10-1/2-in.-diameter glass reactor.

* The relative borohydride concentration was the same as that for the 1/10-scale tests listed in Table 3.

TABLE 5. RESULTS OF HYDROGEN-GENERATION TESTS TO ESTABLISH CONDITIONS FOR OPERATION AT LOW TEMPERATURES

Run No.	Scale	Reaction Solution: $NaBH_4$, lb	Reaction Solution: Water, gal	Reaction Solution: Depth, in.	Temperature, F: Initial	Temperature, F: Rise	Catalyst: Am't, lb	Catalyst: Vol of Solution, gal	Total Generation Time, min
13	1/10	10.0	40	6.4	35	79	3.1	0.5	86
14	1/10	10.0	25	4.1	33	114	3.1	0.5	10
15	1/5	20.0	50	8.2	34	112	6.3	1.0	32
16	1/5	20.0	50	8.2	50	104	2.5	1.0	15
17	1/5	20.0	50	8.2	43	113	4.0	1.0	12
18	Full*	100.0	250	8.2	36	121	23.0	5.0	15
14A	Small	0.6	1.5	4.0	33	98	0.19	-	15
14B	Small	1.2	3.0	8.0	31	102	0.37	-	24
16A	Small	1.2	3.0	8.0	51	91	0.15	-	30

* The measured lift was 223 lb (exclusive of the weight of the balloon and valving).

full-scale generation; Run 18 represented the full-scale test which was performed to check the new catalyst-temperature relationship.

Runs 14A and 14B, and 16A were exploratory, bench-scale experiments conducted at the same relative borohydride and catalyst concentrations as those in Runs 14 and 16, respectively. These runs are discussed below.

Discussion

In the course of carrying out this program, there were two "surge" problems which were of concern. It was possible that the initial reaction between cobaltous chloride and sodium borohydride would evolve a large, perhaps unmanageable, amount of hydrogen when large amounts of catalyst were used. It was also thought that an increase in the concentration of borohydride for low-temperature operation would introduce a large over-all temperature rise in the system and that this would cause an extremely rapid increase in the generation rate during the last 30 to 40 per cent of the reaction. The results showed, however, that, although both of these effects occurred, the surges were not unmanageable and were handled very easily and smoothly in a full-scale generation, as described later.

Data in the chemical literature on the solubility of cobaltous chloride indicated that a maximum of 40 lb of catalyst could be contained in 5 gal of catalyst solution at these low temperatures. As a result, some of the initial experiments of the Phase III study were based on the 40-lb full-scale value. When it was realized that this value was erroneous, all additional experiments were designed around a maximum solubility of 35 lb of catalyst. Runs 3, 8, and 9 (Table 3), which were designed around the 40-lb maximum solubility, showed that with 40 lb of catalyst (i.e., if the catalyst solution were warmed or the amount of solution was increased to 6 gal), the 560-gal unit could be used down to approximately 40 F for generation times of 60 min or less.

The variation in total generation times for Runs 10, 13, and 14 (in Tables 3 and 5), corresponding to 112 min in a 560-gal pool, 86 min in a 400-gal pool, and 10 min in a 250-gal pool with the same quantity of catalyst and borohydride, suggests that a specific change occurred in the reaction mechanism as the amount of water was decreased. It was thought that the change in the solution depth might be influencing the initial mixing and distribution of the catalyst. The depths of the pool in these runs were 9, 6.4, and 4.1 in. respectively (corresponding to depths of 18, 12.8, and 8.2 in., respectively, in the full-scale generator). Runs 14A and 14B (Table 5) were performed to check the effect of pool depth on the total generation time; as the results show, doubling the depth of the solution did increase the total generation time, but by less than a factor of two. Apparently, below a certain depth, mixing becomes more efficient and the reaction is little affected by the time required to distribute the catalyst laterally from the point(s) of addition. Calculated total generation times based on the rate equation developed in the Phase I program, namely:

$$-\frac{d(NaBH_4)}{dt} = 1.45 \times 10^{13} (CoCl_2) (NaBH_4)^{0.39} e^{-17,500/RT},$$

agreed very well with the experimental total generation times in instances where the borohydride concentration was that of the 250-gal system. As a result of this depth effect, Runs 15, 16, and 17 were carried out as 1/5-scale tests (in which the depth of solution is the same as that in full-scale tests).

These results indicated that, in the course of scaling to larger or smaller units, the pool-depth parameter is more important than the pool-diameter parameter. This conclusion was borne out rather strikingly. In changing from a 10.5-in.-diameter reactor to the prototype full-scale generator (8-ft diameter), the pool volume at constant depth was increased by a factor of about 84, yet the total generation times were all in good agreement with the calculated values. On the other hand, changing the depth of the pool from 4.1 in. to 9 in. in Runs 14 and 10 (corresponding to a change of 8.2 in. to 18 in. on a full-scale basis) increased the experimental total generation time markedly.

The ability of the insoluble cobalt boride* to spread out rapidly across the top of the pool was observed directly in bench-scale experiments. While the catalyst dispersed laterally very rapidly, approximately 1 min elapsed before the solution was uniformly black from top to bottom in the bench-scale experiments, and over 3 min, before the bubbling (gas evolution) appeared to be occurring homogeneously throughout the entire solution.

Although it can be readily understood that catalyst distribution should be less rate-controlling in a shallow pool, it was not clear why the effect, as noted in Runs 10, 13, and 14, was so pronounced. However, it was not deemed sufficiently important to the Task Order No. C program to investigate this effect further.

On the basis of Runs 14 through 17 (Table 5), a catalyst-temperature plot was prepared for the 250-gal unit. This plot, the dotted line in Figure 1, was related to cold-weather generation with a total generation time of approximately 10 to 15 min. It was then thought that this total generation time might possibly be too rapid. Calculations were subsequently made to determine the effect of decreasing the amount of catalyst used by 20 per cent. The results of these calculations were as follows:

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* This is the active catalyst compound which is formed as soon as the catalyst solution is added to the borohydride solution, as described in the "Summary Report on Task Order No. C (Phase II)" dated December 31, 1958.

System: 100 lb of $NaBH_4$
250 gal of water
33 F initial temperature

Amount of Catalyst, lb	Total Generation Time, min
31	16
25	20

Thus, the calculations indicated that a 20 per cent decrease in catalyst concentration would slow down the reaction, but not too drastically. On the basis of these calculations, the catalyst-temperature relation, shown as the solid line on the right side of Figure 1, was obtained.

The results of the full-scale test showed that the catalyst-temperature relationship for the 250-gal unit resulted in a smooth generation of 3,500 cu ft of hydrogen in approximately 15 min. The initial surge was quite evident as soon as all of the catalyst solution was added; but, at no time did it appear even close to "getting out of hand". The "tail end" surge was also evident, but to an even lesser extent than the initial surge. The full-scale test also showed that, under service conditions, the operator would have no problem in determining when the generation reaction is complete. The end of the generation is apparent from the cessation of both the sound of the reaction within the unit and of the motion of the balloon gas-inlet tube.

As a result of the studies carried out under the Phases I, II, and III programs, it is evident that hydrogen generators can be designed and constructed to produce hydrogen under a wide variety of conditions. The chemistry of the sodium borohydride hydrolysis is now sufficiently well understood; consequently, only a relatively small amount of calculation and experimentation should be necessary for the development of other hydrogen generators.

ENGINEERING ACTIVITY

The engineering activity under the Phase III program dealt with the mechanical aspects of the hydrogen generator, and included the repair and modification of the 1/5-scale generator, and the design, preparation, and evaluation of a relief-valve and balloon-connector assembly for the full-scale unit.

Repair and Modification of the 1/5-Scale Generator

In preparation for the 1/10- and 1/5-scale hydrogen-generation tests in the 1/5-scale generator, the unit was inspected and repaired to eliminate gas and water leaks. Also, since several wooden stays which supported the wall of the generator were warped badly or broken, new stays were installed.

To provide for the study of the hydrogen-generation surge problem in the 1/5-scale generator, the gas-exit tube was scaled accurately to that of the full-size unit; as a result of the corresponding decrease in the diameter of the exit tube, the rate of gas flow from the small generator would be reduced and the internal pressure produced by the hydrogen generated by the reaction would be similar to that in the full-scale unit. The modification was made by installing an adapter prepared from two sizes of brass tubing. Fittings were provided on the scaled adapter to permit attaching thermocouple leads and a connection to a manometer. In subsequent generation tests, surge in the 1/5-scale generator was noticeable, but, as confirmed by internal-pressure measurements, the generator was at no time in danger of rupture in these tests.

Preparation and Evaluation of Relief-Valve and Balloon-Connector Assembly

Design and Preparation

In view of the experience gained in the previous full-scale experiment, it appeared that there might be a need for a relief valve which would be located in the system at a place between the generator and the balloon; and also for a connector of some type, to provide for the flow of the generated hydrogen from the generator to the balloon gas-inlet tube (and subsequently into the balloon).

Nonmetallic, low-pressure, large-volume-flow relief valves were not commercially available, so several designs of relief valves were evolved and evaluated. Since it was necessary also to provide a connector between the generator exit tube and the balloon inlet tube, an effort was made to design the relief valve as a part of the connector.

The full-scale generator had been designed to withstand an internal pressure of approximately 0.5 psi; consequently, the relief valve was designed to operate at approximately 0.45 psi. An experimental relief-valve assembly was fabricated with a brass-tube housing, a brass ring valve seat, and a brass free-floating weighted-lid valve. To check out this experimental assembly, air under a 70-psi air-line pressure was let into a closed system incorporating this unit. The valve opened at a pressure of approximately 0.45 psi and, in general, operated satisfactorily. However, the size of the weight needed (on the lid of the valve) and the necessity of maintaining the valve in a near-vertical position on the fairly flexible generator led to distinct problems.

In an effort to reduce the size of the weight on the valve and to improve its reliability, the weight in the experimental valve (lid) was replaced by a spring; also, a free-floating lightweight lid was incorporated in the spring-loaded relief valve. The operation of this valve in the test housing was quite satisfactory. The valve was operable and reliable regardless of the mounting position.

The compactness of this experimental valve made it possible to incorporate the valve assembly into the design of the balloon connector. The balloon connector was a T-shaped rigid plastic unit made from short lengths of 5-in.-diameter Plexiglas tubing. One open end was to be inserted in the full-scale-generator gas-exit tube, and the balloon inlet tube was to be attached to the second open end; the relief valve was located in the third open end of the T-shaped unit. The relief-valve and balloon-connector assembly, in position in the generator, is shown in Figure 2. Drawings of the assembly are included in Appendix 1.

Evaluation

The relief-valve and balloon-connector assembly was installed in the full-scale generator, approximately 560 gal of water were added, the balloon-connector opening of the assembly was closed and sealed, and the unit was pressurized internally at approximately 0.45 psi. The relief valve opened and fluttered to allow air to escape, and the internal pressure of 0.45 psi was maintained. The amplitude of movement of the valve as the air escaped was a function of the volume of air flowing through the valve. The full-scale generator ballooned considerably at an internal pressure of 0.45 psi as shown in Figure 3; however, the unit, containing 560 gal of water, was found to be quite stable while resting on dry land.

It was estimated that, during the hydrogen-generation reaction in the full-scale unit, the hydrogen might at times be evolved at a rate as fast as about 1,500 cu ft per min. Calculations indicated that with a 6-in.-diameter balloon inlet tube, 50 ft long, and with a 0.5-psi pressure drop in the tube, the flow capacity of the system incorporating the relief valve

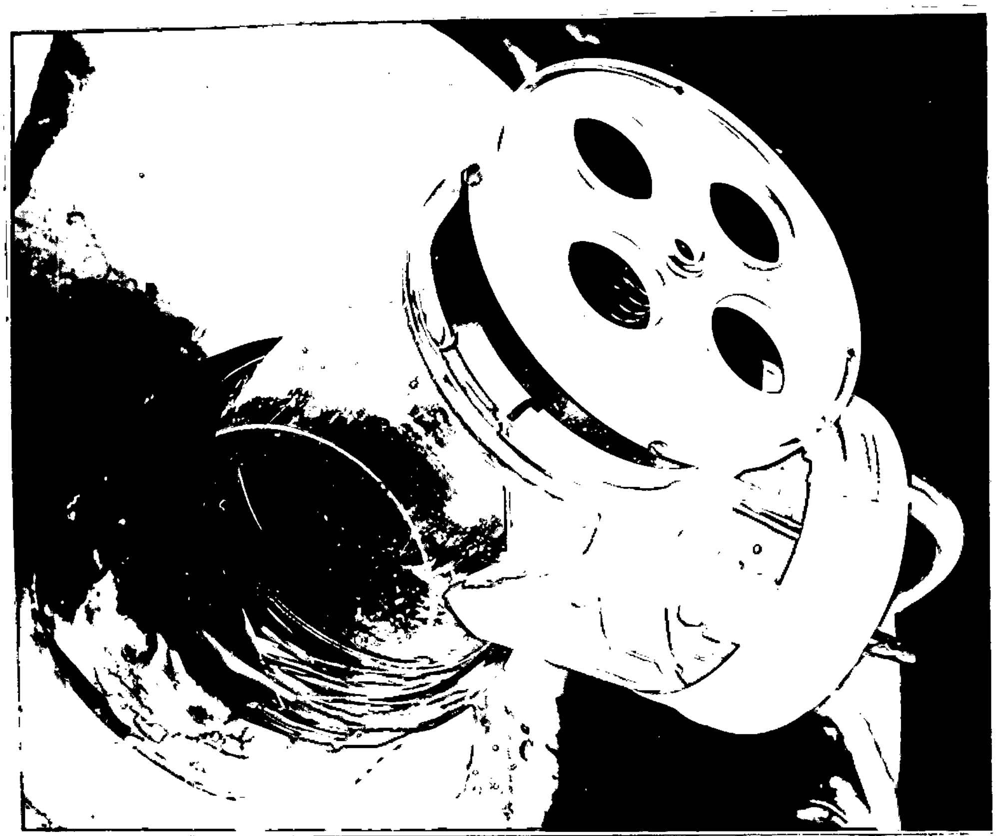


FIGURE 2. RELIEF-VALVE AND BALLOON-CONNECTOR ASSEMBLY IN POSITION ON GENERATOR

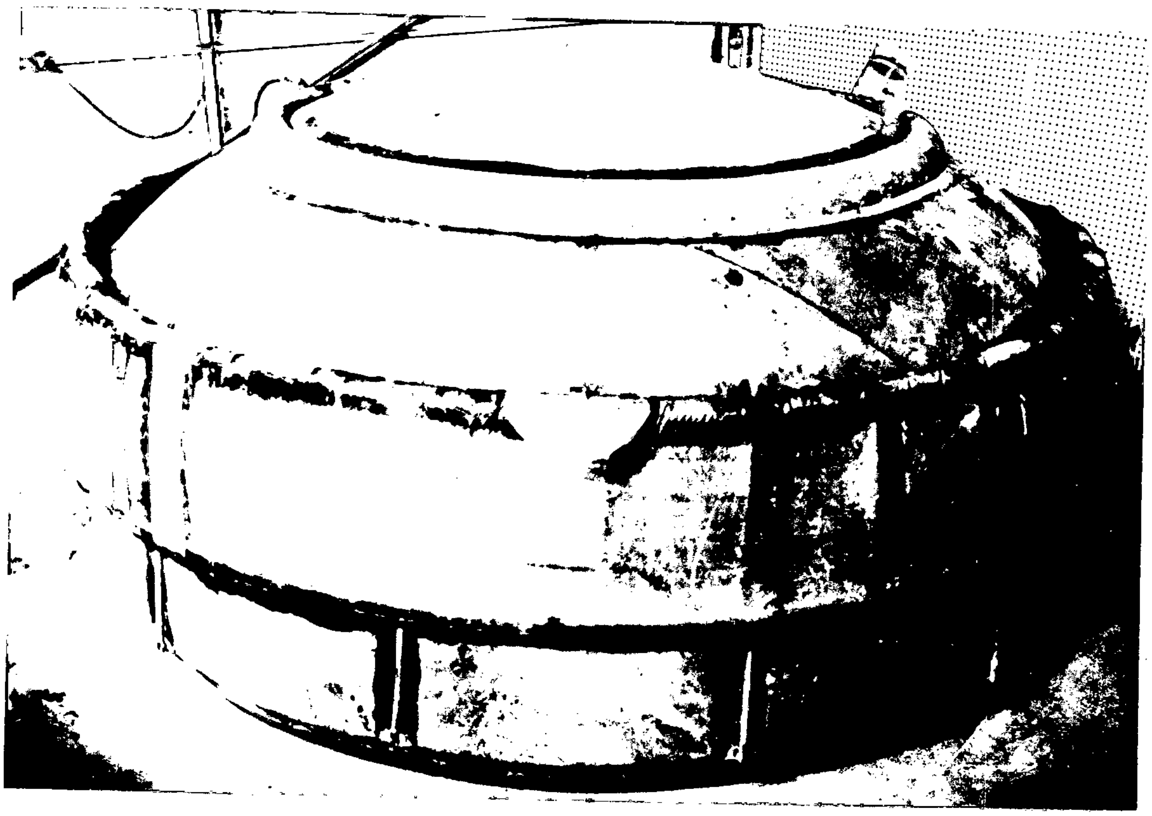


FIGURE 3. FULL-SCALE HYDROGEN GENERATOR WITH RELIEF-VALVE AND BALLOON-CONNECTOR ASSEMBLY INSTALLED AND WITH AN INTERNAL PRESSURE OF 0.45 PSI

could accommodate, theoretically, the flow of hydrogen at a rate of 4,000 cu ft per min.

In preparation for this evaluation, the relief-valve and balloon-connector assembly had been inserted into the generator exit tube and initially sealed in place with plastic electrical tape. However, at low temperatures, this tape becomes brittle and its usefulness is impaired. As a result, adhesive tape was used for this purpose in the full-scale test, and was found to be quite satisfactory.

In regard to the problem of attaching and sealing the relief-valve and balloon-connector assembly to the generator exit tube and also to the balloon inlet tube, the use of metal clamp bands was considered to be objectionable because these would permit the operator to readily apply enough pressure so as to break the plastic connector. Also, the use of metal in the generator kit was to be kept to a minimum, in order to decrease radar detectability. It was felt that plastic clamp bands lacked the necessary strength and reliability, especially for use in the connection to the generator exit tube where the material consisted of several thicknesses and was difficult to seal. O-rings used as clamps were inadequate. The combination of a wide natural-rubber band plus an O-ring clamp was found to be relatively effective. A webbed-fabric draw-up band used with the rubber band was considered to be a more desirable combination. The rubber band would make the seal; the webbed-fabric band would provide for holding the connector in place so as to prevent it from being dislodged from the generator, and also for maintaining the connection between the balloon inlet tube and the plastic connector. However, the elastic bands probably would deteriorate in storage.

Therefore, it appears that adhesive tape should be provided in the kit because taping the joints with this material provides a reliable seal and method of attachment. Also, adhesive tape is satisfactory when using the generator in cold weather, at which temperatures other types of tape become brittle and ineffective.

Study of Method of Adding Water to Generator

During consideration of the various problems of filling the generator with water, it became evident that, at times, it might be necessary to put the water in manually. Thus, if the generator were sitting in water which was too shallow or on dry land, a device such as a bucket would have to be used to obtain the desired volume of water in the generator.

With these needs in mind, a cursory experiment was run to determine how much water could be bucketed by one man in a continuous effort and how fatigued he might become under these conditions. A 2-gal (nominal) bucket was used and the experimenter stood in water which came to a level just above his knees. The bucket was of light plastic material and had a hand grip on the bottom; this grip proved to be very helpful. By bucketing water from one side of a narrow surface, which was about 18 in. above the water, to the other side, the experimenter simulated filling the generator manually.

Under these conditions, it was possible to bucket 600 gal of water in just over 15 min. The experimenter was a person who is an average type of office worker (sedentary worker); while he was tired at the conclusion of the experiment, the effort did not cause significant discomfort.

FUTURE WORK

The use of the prototype generator on land and in water has been demonstrated, and the present design of generator has proven to be quite satisfactory. However, as suggested by your technical representative, the full-scale generator might be improved by eliminating the metal wall supports or stays, in order to decrease further the over-all weight and the radar detectability. Also, when the unit is used in water, the weight is supported by the fabric bottom, which assumes a cone shape and thus pulls in the peripheral wall. If the wall was prepared entirely from the air-mat section, the metal stays could be eliminated, and the unit would assume a more satisfactory shape in the water because it would float on the surface and the wall would be fully supported. Also, following field evaluation of the full-scale generator, there would probably be other design changes to be considered.

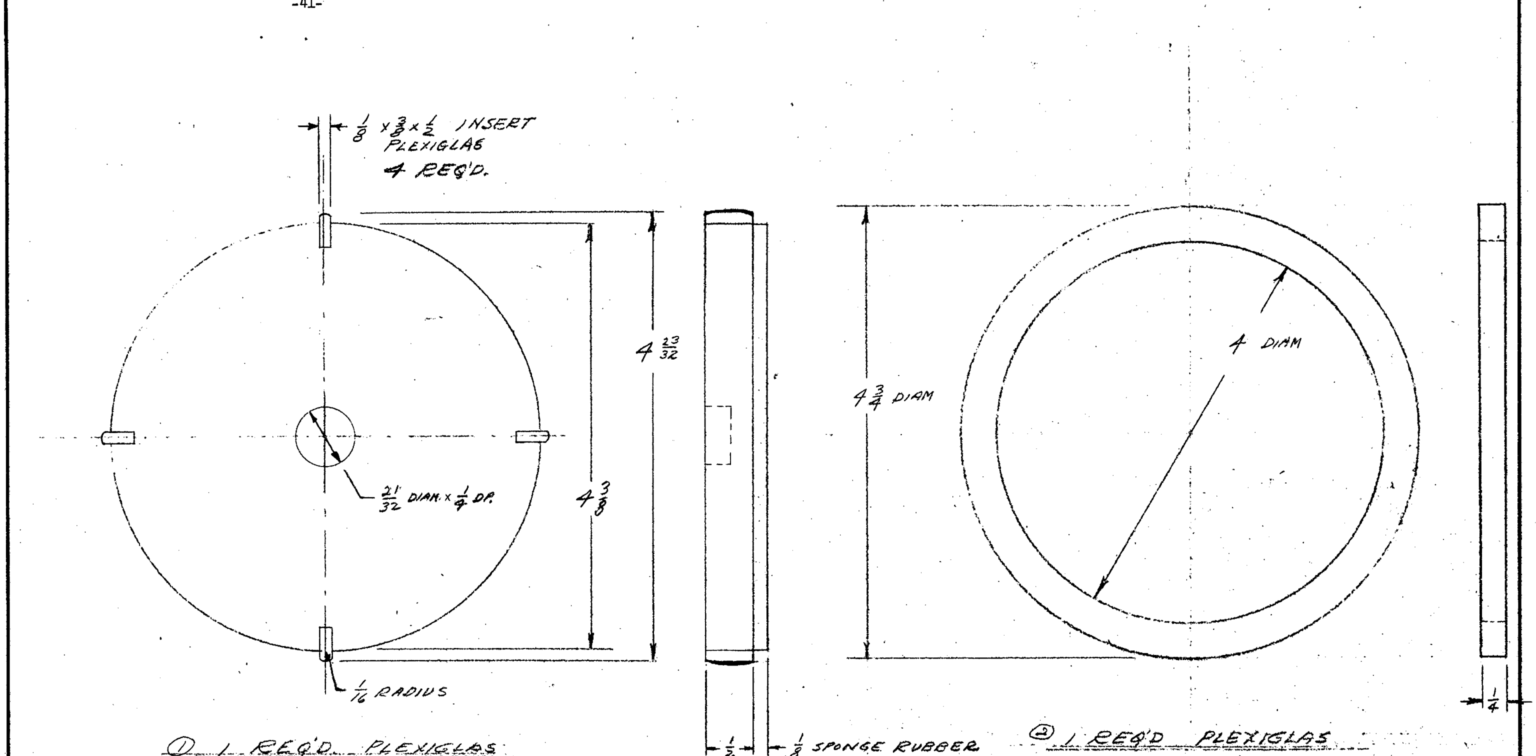
In addition, a water-filling device of some type would be helpful in decreasing the time and/or effort involved in filling the unit with either 250 or 560 gal of water. This device should be capable of appropriately filling the generator either on dry land or in the water.

This study (Phases I, II, and III) has enabled us to develop an understanding of more of the chemistry of the hydrolysis of sodium borohydride than had been previously known. If it should become necessary or advantageous to generate 3,500 cu ft or even larger quantities of hydrogen from a physically smaller unit, this could now be achieved with a minimum of development effort.

APPENDIX 1

DRAWINGS OF RELIEF-VALVE AND
BALLOON-CONNECTOR ASSEMBLY

B



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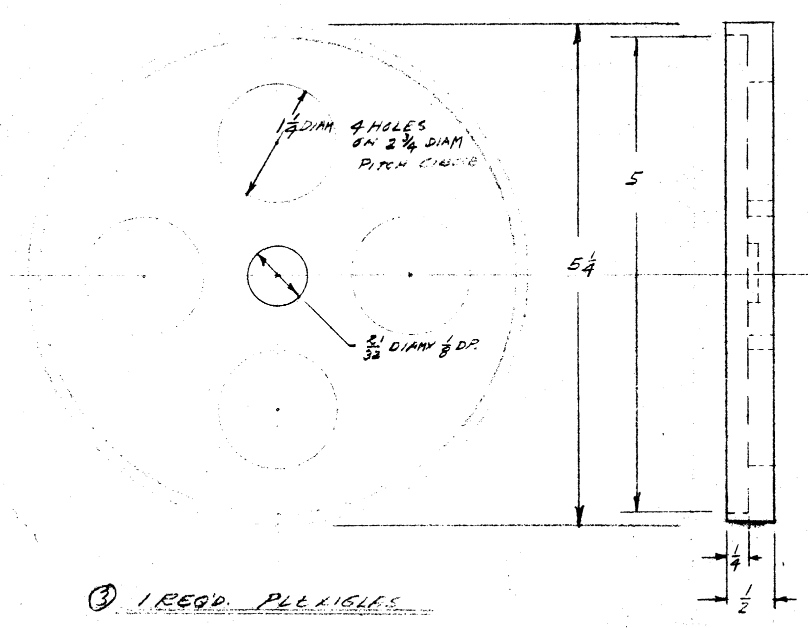

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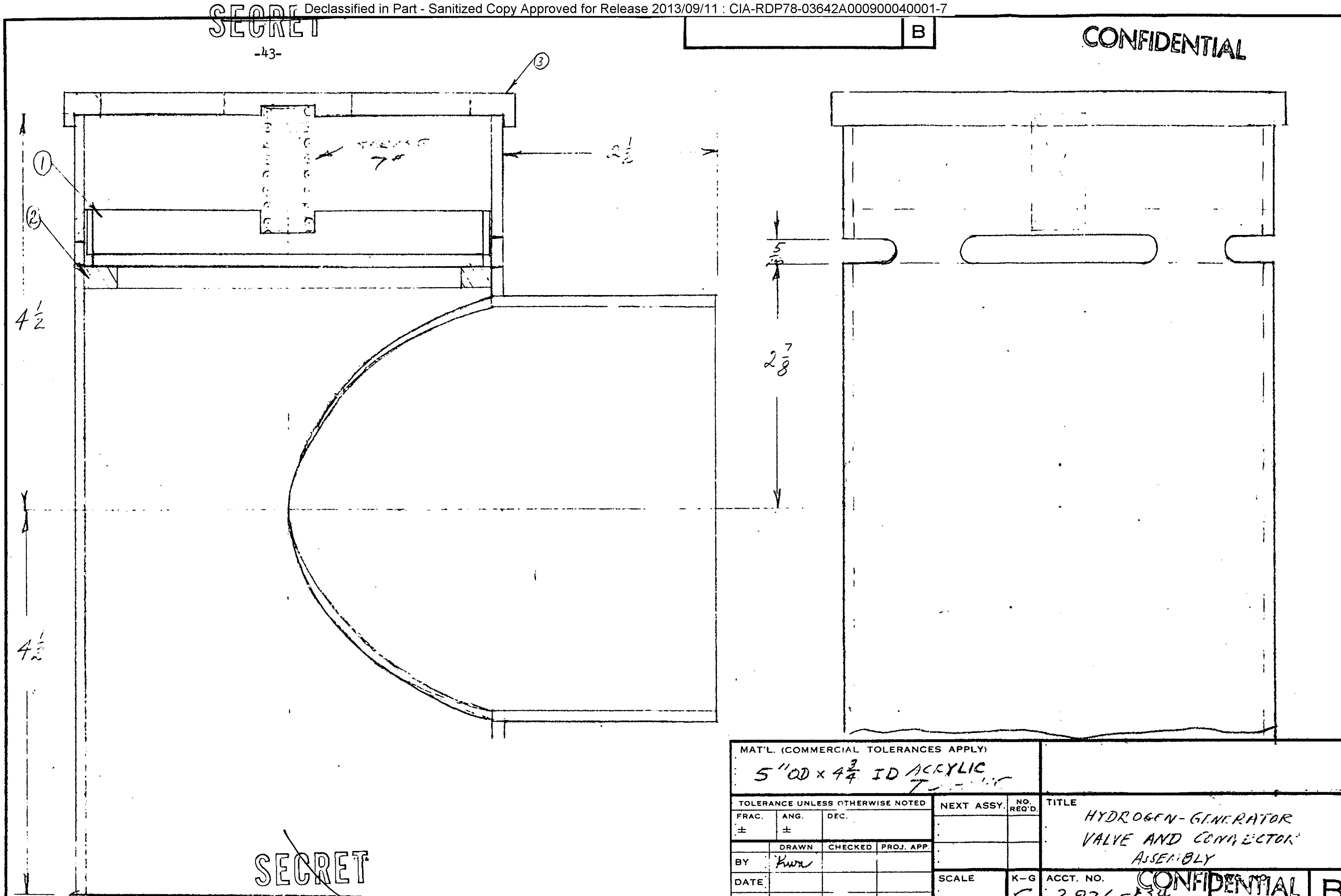

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