OPERATION OF URANYL NITRATE WATER BOILER REACTORS WITHOUT RELEASE OF RADIOACTIVE GASES

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Characteristics of Water Boilers

Among the earliest and simplest types of nuclear reactor developed was the aqueous homogeneous or Water Boiler reactor. A water boiler consists simply of a critical mass of an aqueous solution of a uranium salt, with appropriate container, provision for heat removal, and control elements. Due to the large coefficient of expansion of water, these reactors are largely self-regulating, and are inherently very safe.

Because of their simplicity, very low critical mass, and the absence of fabricated fuel elements, water boilers can be made very cheaply. The containing shell and auxiliary equipment are all made by conventional methods fromcommonmaterials. Their only rival in price in the range up to 50 kilowatts is the Argonaut reactor. The choice between the two may lie in the use to be made of the reactor, and the fabrication facilities available.

Since the first water boiler, called LOPO[1], went critical at Los Alamos in 1943, water boilers have been in operation nearly continuously. The later HYPO and SUPO reactors at Los Alamos were followed by the Raleigh Research Reactors and the Atomics International WBNS, KEWB and commercial models[2]. The culminating achievements in aqueous homogeneous reactors were the Oak Ridge Homogeneous Reactor Experiments 1 and 2 and the Los Alamos Power Reactor Experiments I and II. About 17 water boilers are now in operation in various parts of the world. The successful operation of the HYPO reactor, with 14.5% enriched uranium, and those at Frankfurt and West Berlin, with 20% enrichment, showed that water boilers could be operated at U^{235} concentrations permitted export by the U.S.A.E.C.

The SUPO reactor alone has enjoyed trouble-free operation since 1950, representing 350,000 kilowatt-hours of operation, or of the order of

20,000 hours critical. In that time it has not been necessary to replace or purify the fuel solution[3], the only service being the occasional addition of nitric acid to replace nitrogen lost through radiolytic decomposition of uranyl nitrate.

The most important complicating factor in water boilers, as compared with those having sealed fuel elements, is the decomposition of water, and nitrate ion if present, by fission recoil bombardment. The recombination of hydrogen and oxygen to reconstitute water by a platinized alumina catalyst in an external loop[1] is a well-established technique (Fig. 1), which has been operated continuously for many years in several water boilers. The endothermic oxidation of liberated nitrogen, however, presents more of a problem. Although the use of nitrogen fixation methods for recombining water boiler nitrogen has frequently been suggested[1,4], no evaluation has been presented of their applicability to water boilers.

It was largely because of the lack of a method for suitably disposing of the nitrogen and oxygen produced in uranyl nitrate water boilers that this type of solution, so successful in the HYPO and SUPO models, was abandoned for uranyl sulfate or uranium phosphate solutions in most of the later reactors. Only at an isolated location like Los Alamos is it permissible to release reactor gases to the atmosphere, even after due decay and dilution.

The choice of sulfate instead of nitrate solution at Raleigh led to painful experience, first with the precipitation of uranium peroxide[5], and finally with leaks due to corrosion of the container, which necessitated replacement of the core and subsequent operation at reduced power[2]. The redissolution of the peroxide was made difficult by the fact that the corrosive action of sulfuric acid on stainless steel forbade its addition to the fuel solution.

These problems, at least, are simplified by the use of uranyl nitrate fuel. Even with a considerable excess of nitric acid, these solutions do not attack stainless steel. They have also been operated accidentally under nominally basic conditions[1], when the nitrate ion was so depleted that the uranium must have been largely present in such ions as $U_2O_5^{++}$, rather than the usual UO_2^{+}. When uranium precipitated under these conditions, it was a simple matter to redissolve it with added nitric acid. Uranium peroxide has never been known to precipitate under any normal operating conditions in a uranyl nitrate water boiler. Fission product

nitrates would have less tendency to precipitate than the corresponding sulfates. Such precipitates apparently do not occur, however, even in sulfate research reactors[6]; and in any case would probably not be a serious concern, as their characteristic negative temperature coefficients of solubility would lead to their depositing elsewhere than on the cold heat transfer surfaces. The advantages of nitrate over sulfate solutions particularly at higher powers and temperatures, have been summarized by Marshall[7].

Both uranyl nitrate and uranyl sulfate water boilers have their advantages. The present paper, in presenting alternative methods for handling the products of nitrate decomposition, will permit more effective evaluation of uranyl nitrate water boilers, as compared with other types of reactors, than has hitherto been possible.

Calculations

It was shown by the author[8] that the yield G_{N_2} of nitrogen molecules per 100 electron-volts absorbed by a solution, increases with nitrate concentration. Sowden[9] found this increase approximately proportional to $(NO_3^-)^{3/2}$, and independent of cations present. As water boiler yields were systematically higher than the others considered, conservatism in calculation suggested the derivation of an equation of the same form, but based only on water boiler data:

$$\log G_{N_2} = 1.70 \log (NO_3^-) - 2.32$$

It is found that the volume of nitrogen produced in the concentrated nitrate solution of the HYPO model was thirteen times that from the present SUPO reactor, when compared at the same power level. For economy in gas disposal or recombination, it may be worth while using the greatest possible enrichment. For this reason, the above equation was used to predict the characteristics of a hypothetical reactor having 20% enrichment, the highest permitted export by the U.S.A.E.C. The comparative behaviors of the three reactor models are presented in Table I.

Standard conditions were assumed to be operation at 25 kilowatts thermal for 8 hours a day, 20 days a month. The latter figures were needed to calculate the number of traps required to absorb the off-gases, and the resulting activity levels there.

TABLE I

Off-Gas System Requirements for Water Boiler Reactors Having Different Nitrate Ion Concentrations:-

	Reactor Type		
	HYPO	20% Reactor	SUPO
Uranium enrichment, percent	14.5	20	88
Molarity of nitrate ion	3.84	2.88	0.74
G_{N_2}, molecules/100 ev.	0.047	0.023	9.0036
Nitrogen, gram-moles/sec	1.08×10^{-4}	0.52×10^{-4}	0.083×10^{-4}
$N_2 + 5/2\ O_2$, liters/8 hours	240	120	19
Volume of one-day delay tank, lts.	300	150	23
Time to fill Ca trap, days	7.5	16	98
Ca traps required (adding HNO_3)	9	5	2
Make-up, cc 18 N HNO_3/8 hours	350	170	27
Water to tanks, cc/8 hours	190	90	15
Ca traps required (adding NO)	3	3	2
Make-up, cc NO/sec	4.8	2.3	0.19
Rare gas evolution, cc/8 hours	0.2	0.2	0.2

Recombination of Nitrogen

The gases from the core of a water boiler normally pass through a cooled stack, where water vapor is removed, then through a filter trap to a centrifugal pump. The hydrogen and oxygen from water decomposition are recombined on platinized alumina, and the water separated from the remaining gas in a condenser, after which both water and residual gas are returned to the core[1]. In the SUPO reactor, pressure slightly under atmospheric is maintained by a duct to a stack opening at a point after the condenser exit.

For closed operation with nitrogen recombination the gases, instead of returning to the core after the condenser, would be circulated on through a nitrogen recombining assembly. A typical apparatus (Fig. 2) would consist of an electric discharge, where nitrogen is partially oxidized to NO, followed by a combined delay tank and scrubbing tower, where the dilute nitric oxide is permitted to react with the excess oxygen present, and is then dissolved by the water returning from the

hydrogen recombiner, according to the overall equations:

$$NO + 1/2\ O_2 = NO_2 \qquad (1)$$

$$3\ NO_2 + H_2O = 2\ HNO_3 + NO \qquad (2)$$

The delay tank or reaction volume is desirable because reaction (1) is third-order, with a half-life of 20 seconds. The dilute nitric acid solution and the residual gases are then returned to the reactor core. Although the ideal of a sealed reactor is approached when both hydrogen and nitrogen are thus recombined with liberated oxygen, it is necessary to consider the stable krypton and xenon formed in fission. Atomics International devised a means for collecting these gases in a variable external volume, and later compressing them into a small cylinder[2], but their commercial models do not have this feature[6]. The small volume involved, about 50 cc. per operating year, is so small as to generate a significant pressure rise only in a time of the order of magnitude of the practical useful lifetime of a given fuel charge, perhaps 30 years. Larger volumes of gas might well be involved in fuel transfer operactions, and could in any case be collected during a shutdown in an evacuated shielded trap, preferably packed with activated charcoal. For simplicity the "off-gas compression tank" of Figure 2 would probably be omitted for a water boiler in the usual range of 100 kilowatts or less.

None of the commercial chemical methods for nitrogen fixation from the atmosphere showed any promise for simple adaptation to nitrogen recombination in a water boiler reactor. The Haber process requires high pressure and pure nitrogen and hydrogen. The cyanamide process gives quantities of waste solid material, which would have to be treated as radioactive. In neither case is the product in the desired pentavalent state.

Although nitrogen combines with oxygen under the action of ionizing radiation, such as ultraviolet or pile radiation, its absorption coefficients for these radiations are so low that only large volumes could absorb an effective amount. High enough pressure should help, but no recombination was detected up to 240 psi of nitrogen plus oxygen in the Parasite Reactor experiment[4]. Pressures of greater magnitude in a recombination system are not generally consistent with simple research reactors.

Many types of electric discharge have successfully been used for fixation of atmospheric nitrogen. Any of them seems to give readily a yield of the order of 1% NO. More refined techniques produce several percent of NO[10], and fixation of up to 25% of the 78% of nitrogen in air in a single pass has been reported[11]. The normal flow through the hydrogen recombiner of SUPO is such that a nitrogen recombiner in series with it would need to produce only 0.1% of NO. As the fixation requirements with a fuel of the composition of HYPO are thirteen times greater, however, the same flow would demand nitrogen recombiner efficiency slightly above the minimum expected.

The Birkeland-Eyde process, operating through an electric arc spread by a magnetic field, with its modifications, seems more adapted to large installations than to the recombination of up to 2 or 3 cc. per second of nitrogen. Electric discharges of up to 10 megacycles, and crossed high- and low-frequency discharges, as studied by Partridge[10], Cotton[11] and others have more appropriate and more flexible electrical inputs.

If a one-percent yield of NO is obtained, the maximum input required of any arc or discharge recombiner varies from 0.01 of the reactor fission heat for a dilute nitrate fuel of the SUPO type up to 0.13 of that nominal power for a stronger solution, as in HYPO. One of the more efficient recombiners might need electricity equivalent to perhaps only one-third percent of the reactor power, even for the HYPO fuel.

It seems entirely practicable to seal a high-frequency arc into a recombining system. The source required for a 25-kilowatt SUPO reactor, would be an oscillator and amplifier of the type used for a 250-watt radio transmitter but would be much simpler, as the usual modulation and frequency stabilization equipment would not be needed. Apparently only a small amount of specific development would be needed to apply this technique to an operating reactor.

Absorption of Nitrogen and Oxygen

Radiolytic nitrogen and oxygen, instead of being recombined, might be totally absorbed in heated traps containing an active metal, of which calcium seems the cheapest and most effective. In this technique, the hydrogen recombination system is not modified. At the exit to its condenser, however, the line which in SUPO leads to the stack, goes instead to a delay tank inside the reactor shield, capable of containing

the nitrogen and accompanying oxygen and fission gases produced in one day's operation (Fig. 3). The tank should be filled with packing to prevent circulation within the tank, and to filter out particles of solid fission products. The best packing would be activated charcoal, which would serve to keep practically all the radioactivity from going farther. Pressure in the tank, and therefore in the reactor core, is controlled by a valve at the exit of the tank, such as a Mercoid valve, which is opened by a set pressure, and closes when another desired lower pressure is reached. Such intermittent operation minimizes wear on the valve seat. The gases go from the valve through a manifold, to one of an array of disposable stainless steel traps containing calcium chips, held at 650°C in electric tube furnaces. It has been shown[12-14] that such a trap will absorb, nearly quantitatively, the nitrogen, oxygen and water vapor which may enter it. The rare gases from fission have a volumetric rate of only 0.2 cc. per 8 - hour day when operating at 25 kilowatts, and are easily accomodated in the voids in the trap.

The purpose of the delay tank is to permit the decay of the most active fission gases and the deposition of most of the long-lived activity permanently inside the reactor shield, in order to evade the handling of more than a trace of residual reactivity when the disposable traps are replaced. Since the total production of fission products is of the order of 2 grams per year, most of which stays in the fuel solution, there is no question of plugging the delay tank with solid matter.

After the gases in the tank have decayed for a day or more, the pressure of further gases evolved in the reactor core causes them to be admitted to one of the calcium traps. The principal radioactive components at this point are I^{131}, Xe^{133} and Kr^{87}, which build up to some 400 curies when 25 kilowatt power is maintained for 8 hours every day.

With reasonable insulation, about 500 watts are required to keep one calcium trap at 650° C. Particularly in the case of the HYPO model, a considerable portion of this heat is supplied by the incoming gases, both from reaction with calcium and from radioactive heating. Only the trap actually being filled need be heated, as absorption will have stopped in the filled traps left to cool radioactively.

Stainless steel traps 5 inches in diameter and 2 feet long, having a capacity of 7 liters, fit in standard heating tubes, and are of a size recommended for nitrogen and oxygen absorption. Such traps complete with calcium absorbent and valve, can be made in quantity for US$80. For ease in handling, the furnaces containing the traps should be under the reactor floor, outside the shield. Ten inches of barytes concrete would be ample shielding for the traps, only one or two of which would be at high activity at any one time.

The number of traps required depends upon the rate at which gases must be absorbed and the tolerable level at which a trap can be detached and replaced. The number of calcium traps thought necessary is that which will permit 60 days of radioactive cooling of each trap before it is necessary to decouple and replace it. After that decay time, a trap is found characteristically to have a total activity of about 1 curie, a level at which it is presumed that the line leading to the trap could be decoupled, preferably at a point shielded from the cylinder itself, and the trap loaded on a shielded cart or otherwise carried to radioactive waste disposal without undue radiation exposure. Essentially no activity is released on decoupling.

Under these conditions, it was found that an array of from 2 to 9 7-liter traps would be required, depending on the form in which make-up nitrogen is added to the reactor, as shown in Table I. The number of traps may be brought below these values by packing the delay tank with activated charcoal, which would eliminate the iodine activity, and perhaps the xenon as well. With nitric acid addition, this would reduce the requirement to between three and six traps, depending upon whether the "20% enriched" or the HYPO model were used. Alternatively, larger traps could be used.

The simplest method of replacing the nitrogen lost to the calcium traps would be the addition of concentrated nitric acid as needed (Table I). Occasional analysis of the reactor fuel would be necessary to establish whether the reactor fuel composition is really as expected.

Although a small proportion of the water added as nitric acid would go to the calcium traps as vapor, most of it must be drained out to avoid too great dilution. For this purpose, a normally full water trap of known volume is placed at the exit of the condenser following the recombiner. This trap is drained, at calculated intervals verified

by analyses, to one of two tanks similar to the calcium traps, and likewise placed beneath the reactor floor. These tanks take much longer to fill than the calcium traps, and the decay time of one of a pair while the other is filling is enough to reduce the radioactivity to a safe level for handling.

A more sophisticated procedure than nitric acid addition, when the location and equipment permit, is to replace the nitrogen in the form of nitric oxide gas. The nitric oxide would oxidize the bulk of the oxygen in the gas space of the reactor, forming nitric acid, and reducing the gaseous oxygen to a proportion equimolar with the nitrogen. This saving of oxygen is significant, as it diminishes calcium trap requirements by more than 60%, reducing the number required even for the HYPO model to only four. Known quantities of nitric oxide can be added by metering its flow rate, checking by weighing the cylinder.

With nitric oxide addition, the excess water traps can be eliminated, although for flexibility in operation it might be desirable to retain one. The design of Figure 3 can be accordingly simplified.

Because of its slow oxidation rate, it is important to provide for oxidation and dissolution of the nitric oxide before it enters the main gas stream of the reactor, as contact with the hot hydrogen recombination catalyst would tend to decompose it to the elements. It should therefore be introduced, together with an appropriate small proportion of the gaseous effluent from the hydrogen recombiner system to supply oxygen, through an absorption column; where, when oxidized, it would be dissolved in the water returning to the reactor core from the recombiner (Fig. 3). For the HYPO model reactor system, requiring nearly 5 cc. per second of nitric oxide, an absorption column having a free volume of two liters should be adequate, and would be more than enough for the more enriched models.

Advanced Water Boilers

Although the principal focus of this paper has been on medium-powered research reactors, water boilers have been notably successful in the range below one kilowatt, and also show promise of application to powers higher than 50 kilowatts. King[1] pointed out that the limiting factors with SUPO were the heat exchanger, the shape of the vapor space and the capacity of the installed recombining system.

As shown by the Los Alamos Power Reactor Experiment - II[15], with a cylindrical core and an efficiently designed heat-exchanger there is no reason why water boilers should not operate at several times their present power, without resorting to fuel pumping, as in LAPRE-I and the Homogeneous Reactor Experiments. The preliminary data of Figure 4 were obtained by equilibrating uranyl nitrate solutions with precipitating UO_3, taking a liquid sample[16], and analysing for uranium and nitrate. It was found, as expected, that the addition of excess nitric acid inhibits the hydrolysis of uranyl nitrate characteristic of higher temperatures. It thus seems that the operation of a nitrate water boiler might be practicable at temperatures above 300ºC, should that be desirable to improve heat transfer.

Uranyl nitrate solutions apparently do not undergo decomposition into two liquid phases at high temperatures as do sulfate solutions.

The curves of Figure 4 show distinctly higher acid requirement, especially at higher temperatures, than does the more complete study of Marshall[17], where a similar technique was used. Both sets of observations predict adequate stability of acidified uranyl nitrate solutions for operation of water boilers up to 350ºC. The successful use of a titanium bomb by Gill and Marshall[18] in these determinations indicates that the problem of a container material for use at these temperatures and acidities may be solved. Type 316 ELC stainless steel showed appreciable corrosion by acidic solutions during runs of several hundred hours above 300º.

In the Parasite Reactor experiment[4] a large test bomb containing slightly acidified uranyl nitrate was maintained for several weeks at about 250ºC in the thermal colums of the SUPO reactor, generating a total of 24 kilowatt-hours of heat. No instability of the solution was observed, and the only changes were the characteristic radiolytic decompositions of water and nitrate, with recombination of the water catalyzed by dissolved copper ion.

Conclusion

The techniques introduced and analyzed in this report will make it possible to take advantage of the chemical stability and predictability of uranyl nitrate water boilers to build new low-priced research reactors of a wide range of power levels. The experimental

difficulties with uranyl sulfate water boilers have also now been overcome, and either type is now applicable to populated locations.

Both nitrogen recombination and absorption of off-gases seem perfectly feasible techniques, but the latter has the advantage of using completely known and familiar methods, which should require little or no study to adapt them to water boiler use.

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LIST OF FIGURES

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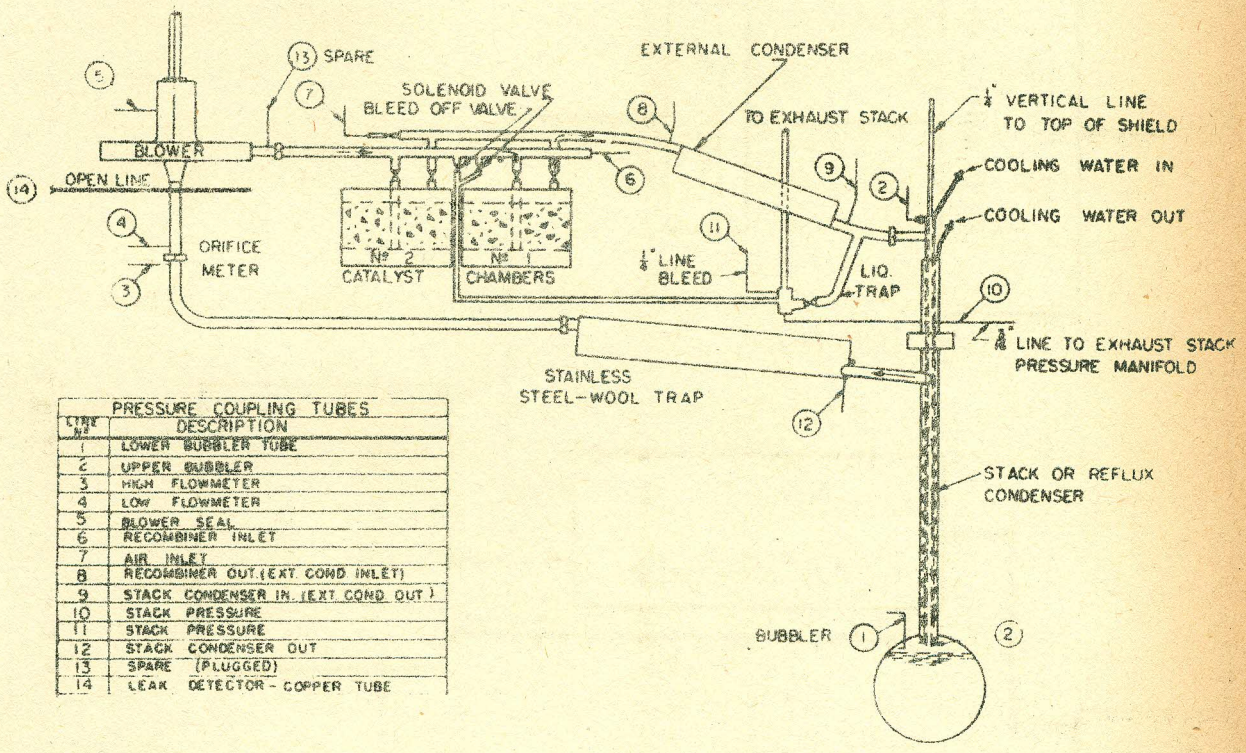

PRESSURE COUPLING TUBES	
LINE №	DESCRIPTION
1	LOWER BUBBLER TUBE
2	UPPER BUBBLER
3	HIGH FLOWMETER
4	LOW FLOWMETER
5	BLOWER SEAL
6	RECOMBINER INLET
7	AIR INLET
8	RECOMBINER OUT (EXT COND INLET)
9	STACK CONDENSER IN (EXT COND OUT)
10	STACK PRESSURE
11	STACK PRESSURE
12	STACK CONDENSER OUT
13	SPARE (PLUGGED)
14	LEAK DETECTOR - COPPER TUBE

FIG. 1

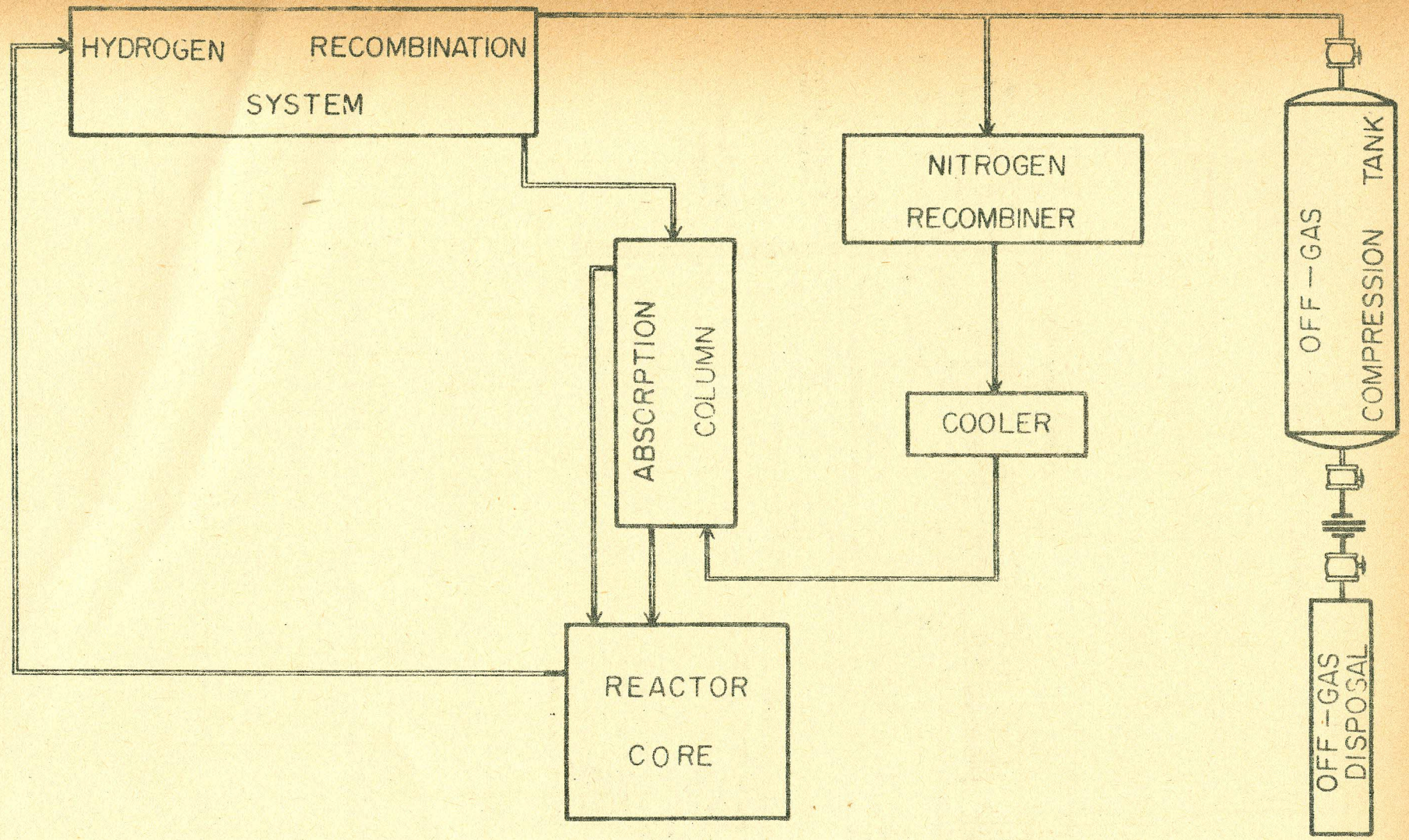
HYDROGEN RECOMBINATION SYSTEM
NITROGEN RECOMBINER
ABSCRPTION COLUMN
COOLER
OFF-GAS COMPRESSION TANK
REACTOR CORE
OFF-GAS DISPOSAL

Fig. 2

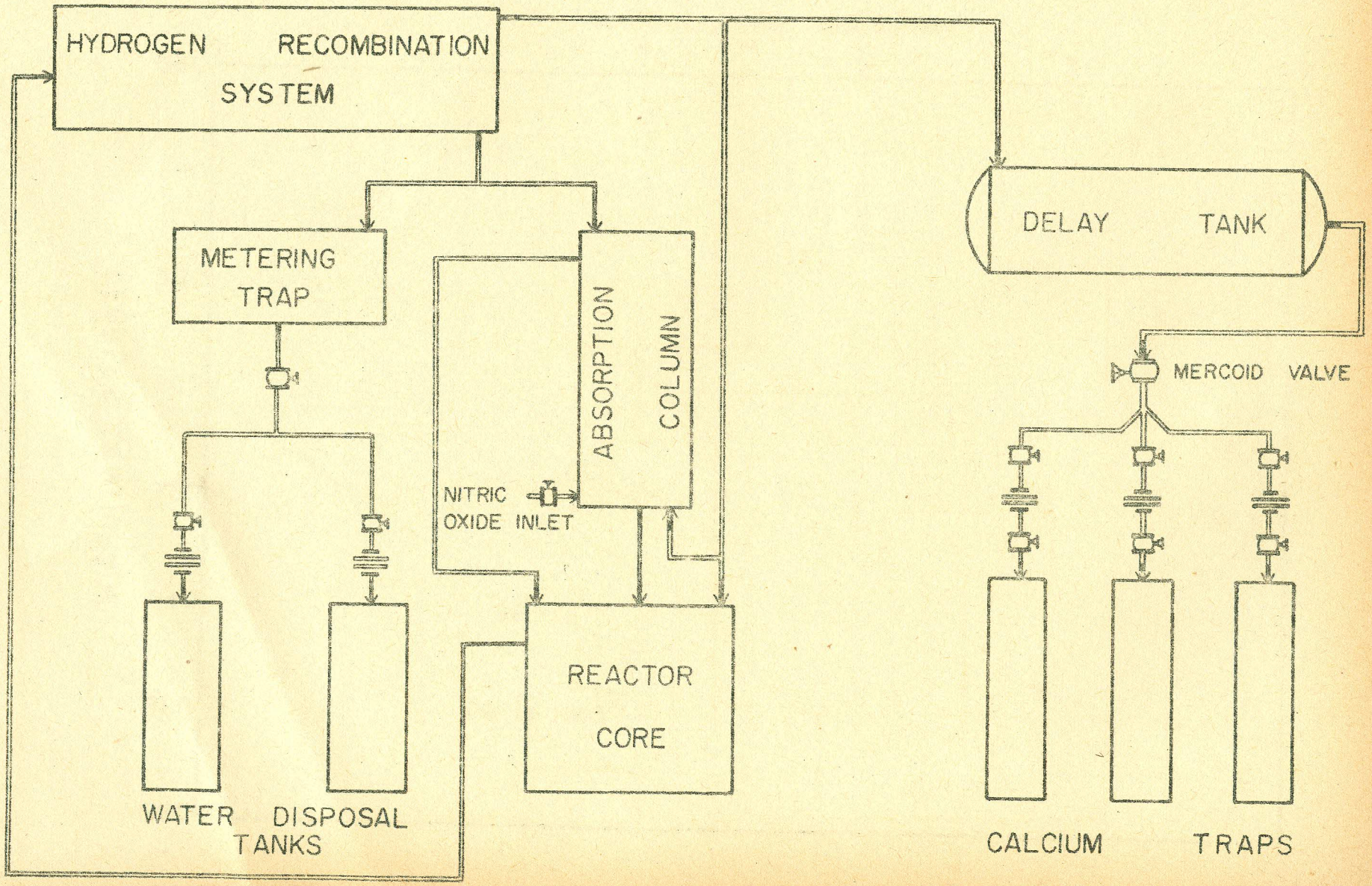
HYDROGEN RECOMBINATION SYSTEM
METERING TRAP
ABSORPTION COLUMN
NITRIC OXIDE INLET
DELAY TANK
MERCOID VALVE
REACTOR CORE
WATER DISPOSAL TANKS
CALCIUM TRAPS

Fig. 3

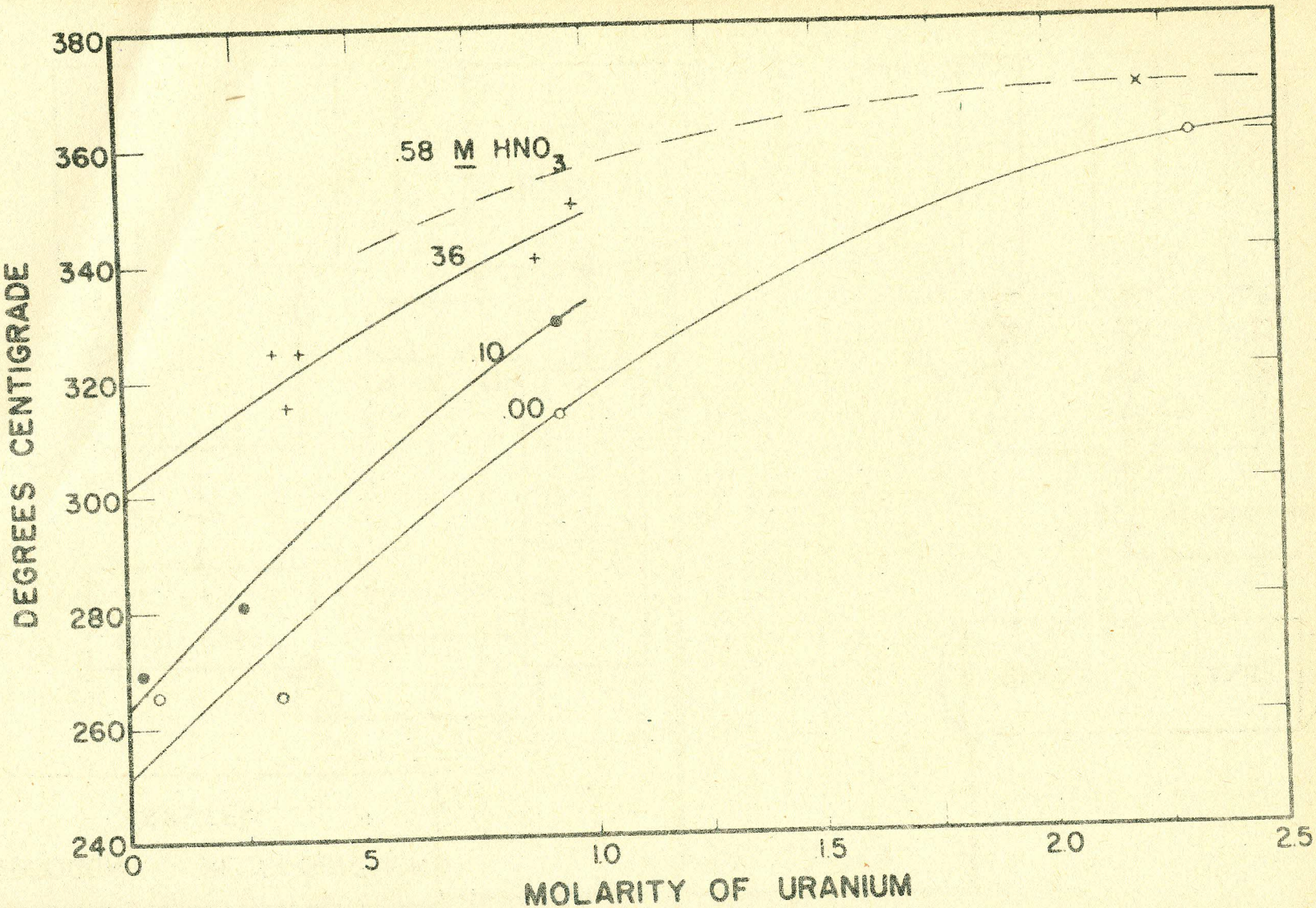
380
360
340
320
300
280
260
240
DEGREES CENTIGRADE
.58 M HNO3
.36
.10
.00
0
.5
1.0
1.5
2.0
2.5
MOLARITY OF URANIUM

FIG. 4