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CHEMICAL TECHNOLOGY DIVISION

CONCEPTUAL DESIGN OF A CONTINUOUS FLUORINATOR
EXPERIMENTAL FACILITY (CFEF)

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ABSTRACT

A conceptual design has been made of a circulating salt system, consisting principally of a fluorinator and reduction column, to demonstrate uranium removal from the salt by fluorination. The fluorinator vessel wall will be protected from fluorine corrosion by a frozen salt film. The circulating salt in the fluorinator will be kept molten by electrical heating that simulates fission product heating in an actual MSBR system.

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1. INTRODUCTION

The present flowsheet for processing a single-fluid MSBR includes a fluorination step for continuously removing 99% of the uranium from a salt stream coming from the reactor at the rate of 3.3 liters/min. The salt stream passes through a reductive-extraction step for protactinium removal, and a metal-transfer step for rare-earth removal before being returned to the reactor. Two smaller fluorination operations are also required for removing uranium from the secondary salt stream that flows to the protactinium decay tank, and for the periodic recovery of uranium from the protactinium decay tank.

Operability of a frozen wall fluorinator using autoresistance power to simulate fission product heating has been tested in three experiments: AHT-2, AHT-3, and AHT-4.[1-4] In experiment AHT-2, LiF-BeF$_2$ salt (67-33 mole %) was used in a simple, vertical test vessel with satisfactory results.[2] In AHT-3, successful runs were made using MSBR fuel carrier salt with the electrode in the vertical test section.[5] In AHT-4, MSBR

fuel carrier salt was circulated through the test vessel, which was similar to a proposed fluorinator.[6] The electrode was placed in a side arm that was connected to the vessel near the top of the vertical fluorination section. No fluorine was used in any of these experiments.

The objective of the continuous fluorinator experimental facility (CFEF) is to demonstrate the actual fluorination of uranium in a circulating salt system that is similar to AHT-4. The uranium that is not volatilized, but which is partially oxidized to UF_5, will be reduced back to UF_4 in a hydrogen reduction column. This demonstration is expected to provide information about corrosion protection by the frozen salt film, and operating experience and process data, including fluorine utilization, reaction rate, and flow rate effects.

2. SUMMARY

The continuous fluorinator experimental facility will be installed in a cell in Building 7503 to provide beryllium containment. The system will contain 8 to 9 ft^3 (0.23 to 0.25 m^3) of MSBR fuel-carrier salt (72-16-12 mole % $LiF-BeF_2-ThF_4$) containing an initial quantity of 0.35 mole % of uranium. The salt will be circulated at up to 100% of MSBR flow rate (3.3 liters/min). Because of the short fluorination height and depending on operating conditions, the uranium that is volatilized will range between 80% and 95%. The variables of salt flow rate, fluorine flow rate, and fluorine concentration will be studied by measuring the UF_6 concentration in the fluorinator off-gas stream, and by sampling the salt stream after reduction of UF_5 to UF_4. Mass flowmeters in the fluorinator off-gas stream before and after the NaF traps will provide a continuous indication of the uranium volatilization rate.

Fluorine utilization can be calculated from the final mass flowmeter reading and the fluorine feed rate. The amount of UF_5 in the stream going to the reduction column can be determined from the fluorine utilization and UF_6 volatilization rates. Another mass flowmeter in the gas stream coming from the reduction column will indicate the unreacted

hydrogen plus the HF which is formed. The reduction efficiency can be calculated from this reading. The fluorinator will have two fluorine inlets to provide data for determining the column end effects. Reduction of UF_5 will be carried out in a gas lift in which hydrogen will be used as the driving gas and also as the reductant. If additional reduction is required, it can be done in the salt surge tank. The surge tank is designed to provide sufficient salt inventory for about 4 hr of fluorination under operating conditions which result in 80% uranium volatilization per pass, and 11 hr of fluorination under conditions which result in 95% uranium volatilization per pass. About 99% of the uranium should have been removed from the salt batch after these periods of time.

3. DESIGN DESCRIPTION

The flowsheet is shown in Fig. 1. Salt will enter the fluorinator through the electrode in a side arm. The electrode flange will be insulated electrically from the rest of the fluorinator, and the autoresistance power will be connected to a lug on the flange. The salt will leave at the bottom of the fluorinator below the fluorine inlet side arm. The fluorinator pipe wall will be cooled by external air-water coils to form the frozen salt film, which serves the dual purpose of preventing nickel corrosion and autoresistance current shorting. Below the fluorine inlet, the fluorinator wall will not be cooled and the molten salt will complete the electrical circuit to the vessel wall. Since all of the uranium will not be volatilized, some partially oxidized uranium will be found as UF_5 at the bottom of the fluorinator. The fluorinator bottom, exit line, and reduction column will be protected from the highly corrosive UF_5 by gold lining (or plating). The molten salt containing UF_5 will enter at the bottom of the column where it will be contacted with hydrogen. The hydrogen will be introduced into the column through a palladium tube; this will result in the formation of atomic hydrogen, which greatly increases the reduction rate of UF_5 to UF_4. The hydrogen reduction column will also act as a gas lift to raise the salt to a gas-liquid separator. The salt will then flow by gravity to the fluorinator through a salt sampler,

TO OFF-GAS

TO FLUORINE DISPOSAL SYSTEM

SAMPLER

GAS-LIQUID
SEPARATOR

HF
TRAP

UF$_6$ TRAPS

HEAT
FLOWMETER

FLUORINE

AUTO-
RESISTANCE
POWER
SUPPLY

SURGE
TANK

REDUCTION
COLUMN
AND
GAS-LIFT
PUMP

FREEZE VALVE

FLUORINATOR

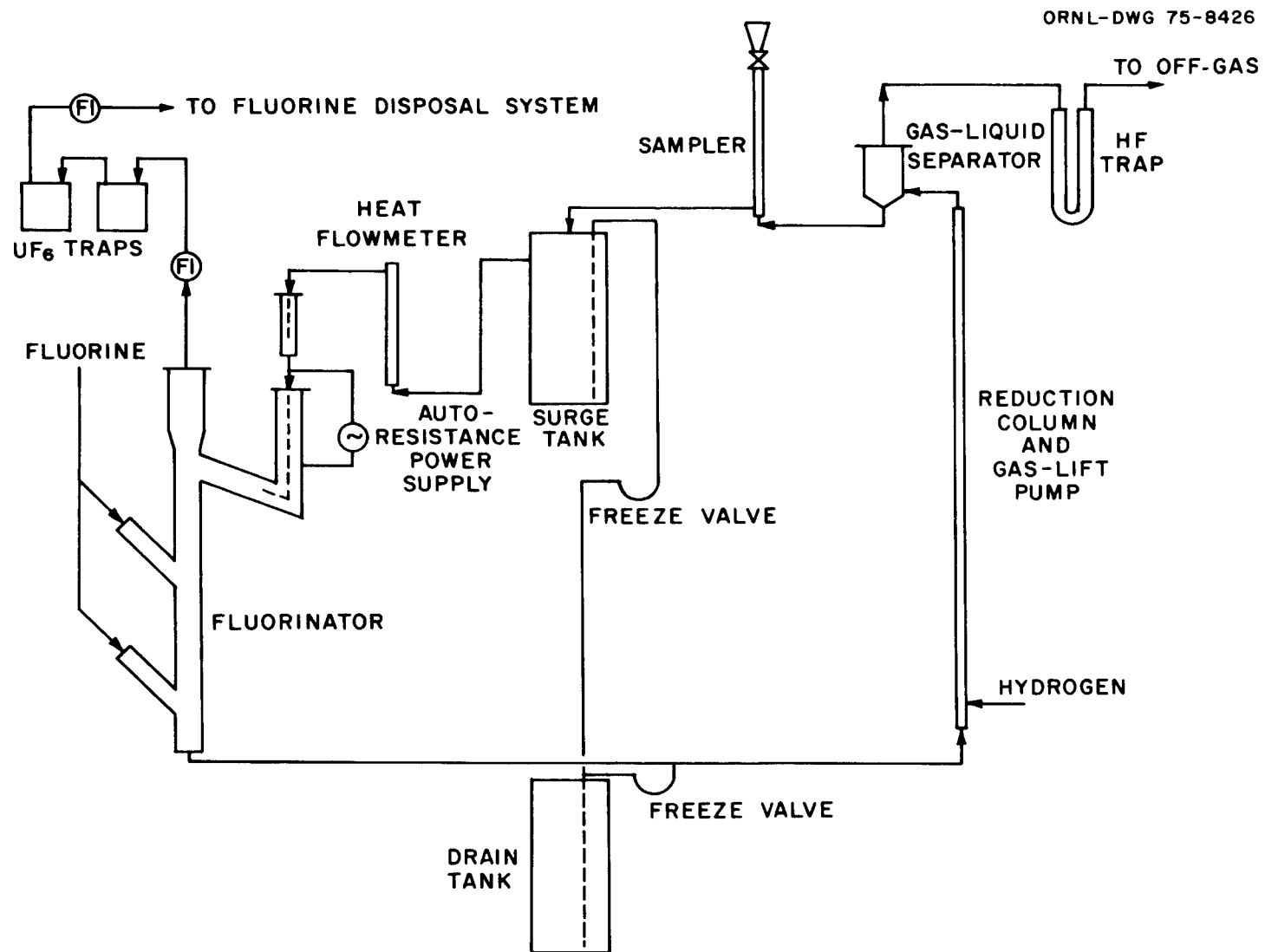HYDROGEN

FREEZE VALVE

DRAIN
TANK

Fig. 1. Continuous Fluorinator Experimental Facility flowsheet.

surge tank, heat flowmeter, and electrical circuit-breaking pot. The surge tank will have a working volume of 5 ft^3 (0.14 m^3), and a dip tube through which hydrogen can be introduced if further uranium reduction is required. Reduction off-gas from the separator and surge tank that contains HF and excess hydrogen will pass through a NaF bed for removal of the HF. The excess hydrogen will be diluted below the explosive limit before being discharged to the cell off-gas.

Off-gas from the fluorinator will contain UF$_6$ and excess fluorine; argon will also be in the off-gas if it is used to dilute the fluorine. The gas will pass through two sodium fluoride beds for uranium removal. Hastings mass flowmeters will be installed upstream and downstream from the beds. The difference between the two readings is a measure of the UF$_6$ flow rate. This provides an instantaneous and reasonably accurate means for determining the fluorine utilization and reaction rate. An engineering layout of the equipment to be installed in the spare equipment cell in Building 7503 is shown in ref. 7. A description of the individual equipment items follows.

Fluorinator. This vessel (Fig. 2) is similar to the test vessel used in experiments AHT-3 and AHT-4; however, several changes have been made based on operating experience. The diameter of the entire vessel was increased from 6 to 8 in. (0.15 to 0.20 m) to simplify frozen-film formation and to provide space for a thicker film, thus minimizing the effect of nonuniform film thickness. The heated jacket over the electrode was lengthened to reduce the danger of the salt freezing in the unheated end. Fluorination zones of 3 and 6 ft (0.9 and 1.8 m) are provided by having two fluorine inlets. Since complete fluorination is not expected, and UF$_5$ (which is very corrosive) will be present in the salt below the fluorine inlet, it will be necessary to cool all five jackets regardless of whether the 3-ft or 6-ft (0.9 or 1.8 m) fluorinator is being used. The bottom of the fluorinator and the line to the reduction column will be protected from corrosion by a gold lining. Contact between the molten salt and this lining will complete the electrical circuit for autoresistance heating.

Alternative fluorinator designs (to the autoresistance heated unit shown) are being considered for the CFEF. The salt core could be kept
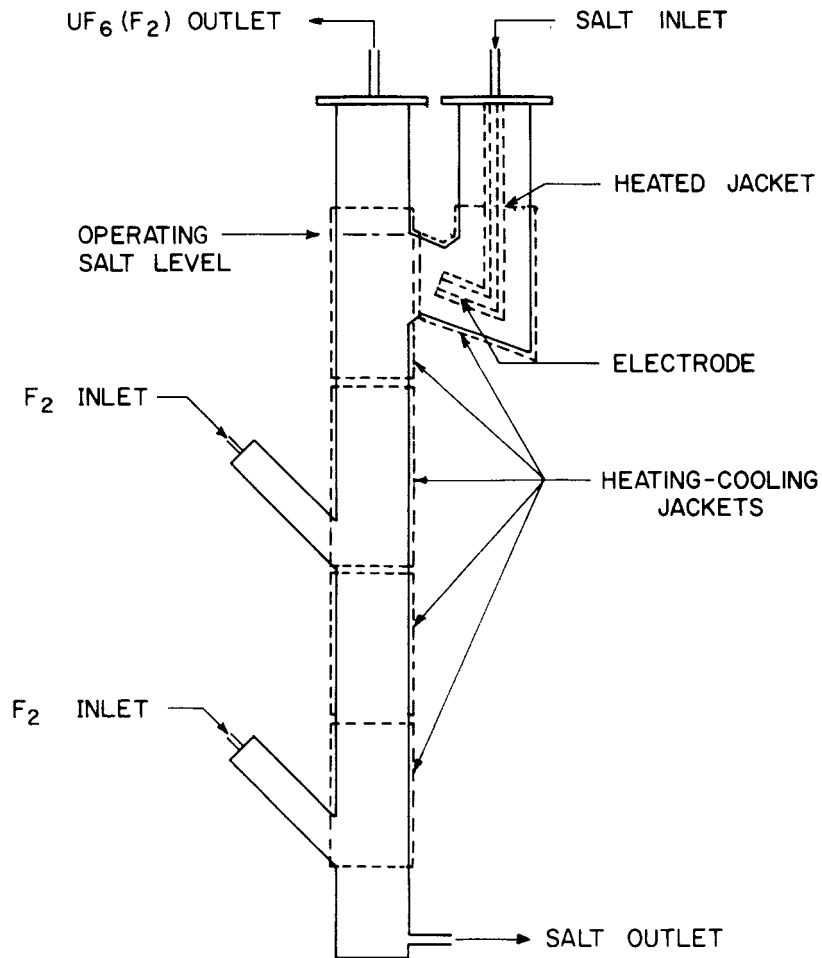
ORNL DWG 76-128

UF$_6$(F$_2$) OUTLET ←   ⌐ SALT INLET

HEATED JACKET

OPERATING → SALT LEVEL

ELECTRODE

F$_2$ INLET

HEATING-COOLING JACKETS

F$_2$ INLET

→ SALT OUTLET

Fig. 2. Continuous fluorinator.

molten by the use of a jacketed axial heater in the center of the fluori-
nator. Although corrosion would be severe (probably $\sim$ 0.03 mm/hr), at
least 100 hr of fluorination should be possible before the jacket fails
and/or the salt is saturated with NiF_2 ($\sim$ 0.9 wt %). It would also be
possible to supply sufficient heat in the entering salt so that the salt
leaving the bottom of the fluorinator will not be cooled below the liquidus
temperature. Figure 3 shows, for example, that the heat loss through a
1-in.- (25-mm) thick salt film could be compensated by a salt temperature
drop of 40°C (inlet-exit) at one-half the MSBR salt flow rate if a 400°C-
pipe wall temperature is desired.

There are disadvantages to these two alternative designs. Corrosion
of the axial heater jacket would consume fluorine and prevent the accurate
calculation of fluorine utilization in the uranium-fluorine reaction.
Without knowing the fluorine consumption in the oxidation of uranium it
would not be possible to calculate the amount of UF_5 formed. If no inter-
nal salt heating is used, the high inlet salt temperature that is required
could cause difficulty in forming and maintaining a salt film near the
electrode. In any case, the salt film would probably be less uniform
than with internal heating, because the film would be thinner near the
salt inlet and thicker near the salt outlet.

Reduction column. Since the reduction column also functions as a
gas-lift to provide salt circulation, the diameter, height, and elevation
will be determined primarily by the gas-lift design. The salt head in
the fluorinator will determine the gas-lift submergence (about 50%),
and the salt circulation rate (1 to 3 liters/min) will determine the
column diameter. The entire column height will probably not be required
to accomplish complete reduction of UF_5. The palladium catalyst at the
hydrogen inlet should provide adequate reduction with a small contact
height. The column will be lined or plated with gold to prevent corro-
sive attack by the UF_5. If additional reduction is required, hydrogen
could be supplied easily through a dip tube in the surge tank to com-
plete the reaction there; however, corrosion from UF_5 could be a problem
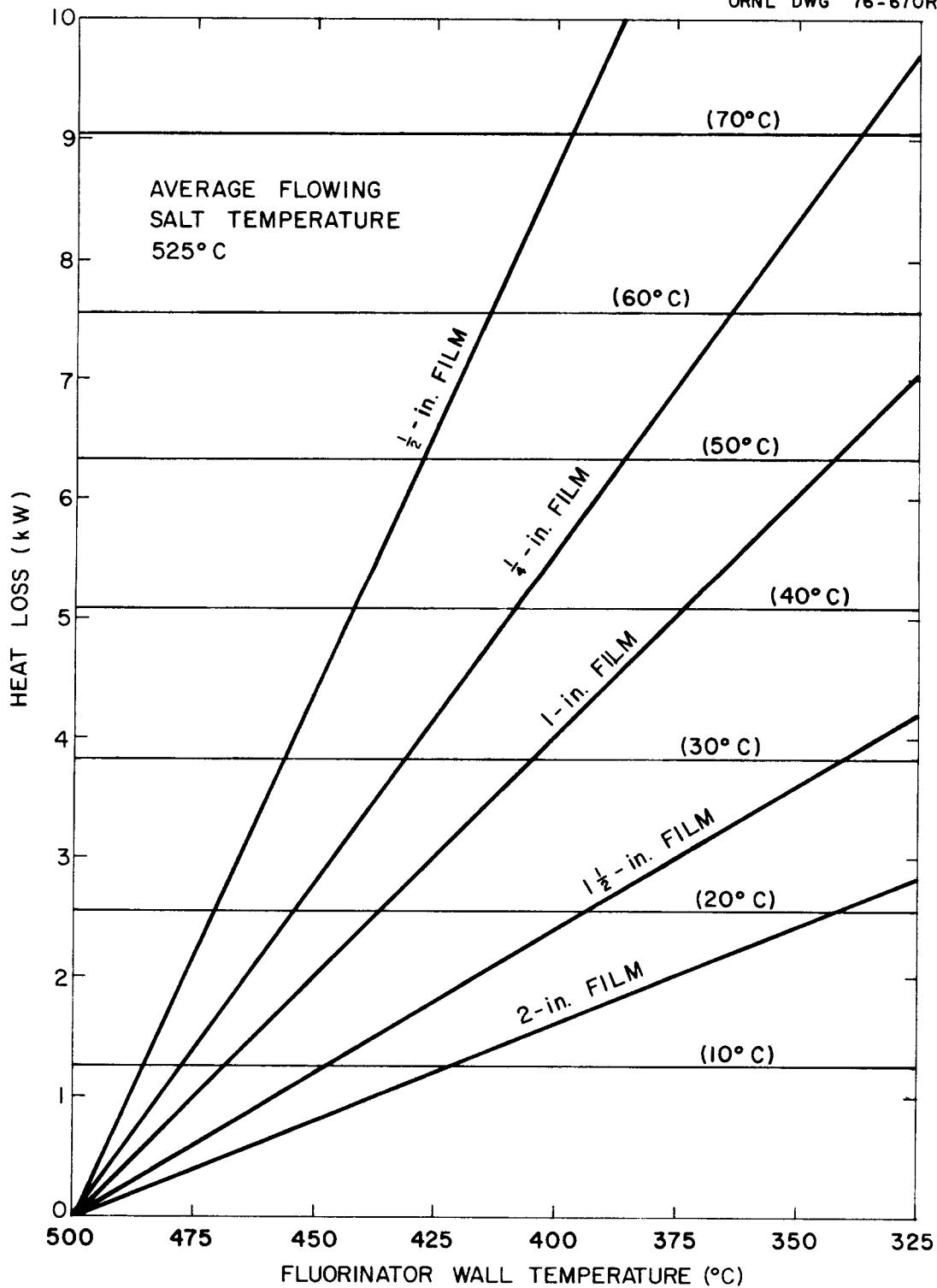since there are no plans to gold line this tank.

Fig. 3. Heat loss from a fluorinator through several thicknesses of frozen salt film as a function of fluorinator wall temperature. Horizontal lines show heat removal from salt flowing through the fluorinator at 1.7 liters per minute [1/2 the processing rate for a 1000-MW(e) MSBR] for the indicated salt temperature change.

Surge and drain tanks. Before being returned to the fluorinator, the salt will pass through a 5-ft^3 (0.14-m^3) surge tank to provide salt inventory. This tank will have a baffle to prevent short circuiting of salt flow from inlet to outlet. Salt overflows from a side outlet, the level of which determines the tank capacity.

The drain tank is similar to the surge tank in size and design and has sufficient capacity to contain the salt volume of the test vessel and reduction column. It will be necessary to drain these vessels periodically for inspection and possible maintenance. The drain tank will be subjected to the greatest pressure in the entire system when salt is transferred back to the circulating system. Design of this vessel must therefore be approved by the ORNL Pressure Vessel Review Committee.

HF trap. The off-gas from the gas-liquid separator and the surge tank will contain HF and excess hydrogen from the UF_5 reduction step. This gas is passed through a NaF bed. The bed depth is 3.3 ft (1.0 m), and has a calculated pressure drop of 0.15 psi (1034 kPa) with a gas flow rate of 1 cfm (4.7 x 10^{-4} m^3/sec). The bed has the capacity to absorb the HF evolved from 1.3-fuel salt batches containing 0.35 mole % uranium, assuming no UF_6 evolution (all UF_4 is converted to UF_5, and is reduced by hydrogen to UF_4). Since absorption is poor at high temperatures, the gas from the reduction step is cooled to 100°C before it enters the trap. Cooling the gas to below 100°C at the inlet would result in a high partial pressure of HF (probably ~ 20%), which would form the higher HF complexes (NaF·2HF, NaF·3HF, etc.) and cause plugging. A cooler is provided on the bed exit to improve absorption at that point and prevent HF release.

UF_6 traps. The absorbers for collecting the UF_6 on NaF pellets are made of carbon steel that is sufficiently resistant to fluorine corrosion at low temperatures. Surplus absorbers from the MSRE fuel processing will be used.[8] One of these absorbers, having a bed depth of 10 in. (0.25 m), contains 24 kg of NaF and has a capacity of about 15 kg of uranium. Less than 10 kg of uranium is contained in 8 ft^3 (0.23 m^3) of fuel salt. The absorbers are designed with an open 2-in. (51-mm) center pipe for air

cooling, although this was not found to be necessary in MSRE operation. The UF_6 flow rate is expected to be much lower in the CFEF.

Sampler. The salt will be sampled after it leaves the reduction column and the gas-liquid separator, and before it enters the surge tank. The sample will be analyzed for total uranium and the oxidation state will not affect the results. The sampler is of the same design that has been used successfully for many years. It is the only piece of equipment extending through the containment cover over the cell. Local ventilation will be required to prevent spread of beryllium contamination.

Circuit-breaking pot. In order to minimize the equipment operating at the autoresistance potential (up to 200 V), a pot will be inserted between the heat flowmeter and the electrode-salt inlet pipe in the fluorinator. In this pot, the salt stream will impinge on a horizontal disk causing a salt spray that breaks the electrical circuit. As shown on the flowsheet (Fig. 1), the pot and fluorinator both have insulated flanges so that only the pot and fluorinator top flange will be at high potential.

Heat flowmeter. The salt leaving the surge tank will pass through a 28-in. (0.71-m) section of 2-in. nickel pipe containing a cartridge heater. Heat loss from the flowmeter will be balanced by external heaters. The salt flow rate can be calculated from the temperature rise of the salt as it passes through the flowmeter and the known power input of the cartridge heater.

3.1 Fluorine Supply System

The fluorine supply system that was used in processing the MSRE fuel salt will be reactivated for use with the CFEF.[9] The system (Fig. 4) has provisions for the connection of two 18-std-m^3 fluorine trailers with safety controls to limit the maximum flow rate and to remotely stop the flow in case of a leak. A NaF trap is available to remove HF from the fluorine. The HF could cause plugging of the UF_6 absorbers by formation of complexes of NaF with two or more molecules of HF. The bed inlet is heated to prevent the formation of these complexes in the trap. Fluorine flow is controlled by means of a control valve and an orifice flowmeter.
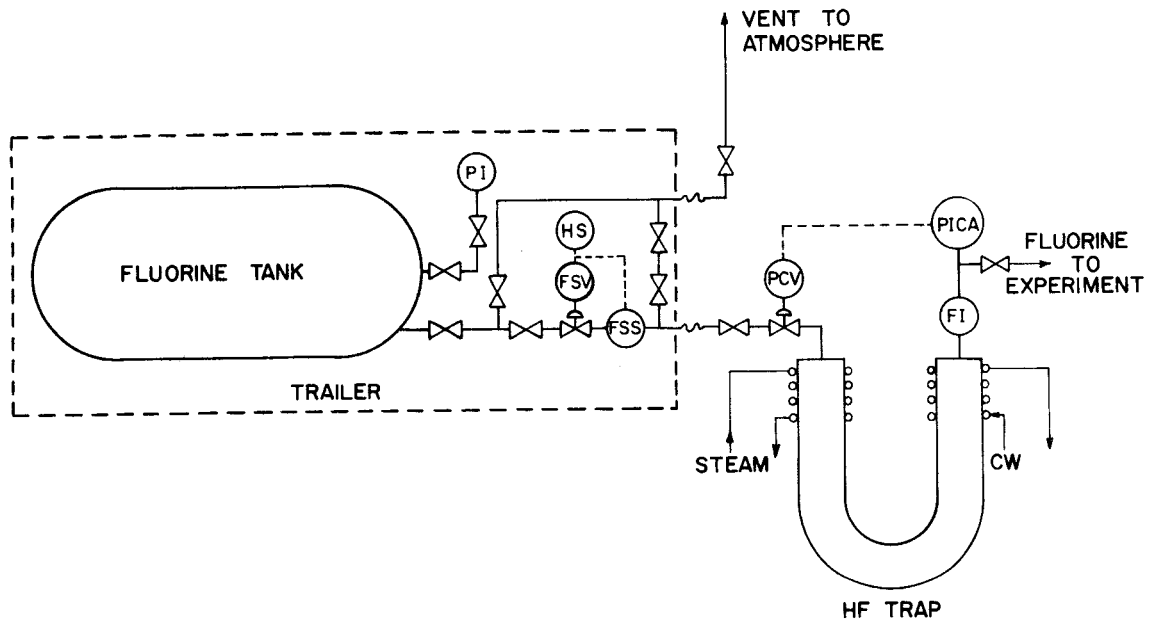
ORNL DWG 76-127

Fig. 4. Fluorine supply system.

3.2 Fluorine Disposal System

The CFEF will be the first test of the frozen-wall fluorinator using
fluorine. A vertical scrubber is being installed in Building 7503 for
the disposal of the excess fluorine. A flow diagram of the system is
shown in Fig. 5. The scrubber is a 6-in., 8-ft- (2.4-m) high Monel pipe
with three spray nozzles in the upper half of the vessel. The surge tank
contains 200 gal (0.76 m^3) of an aqueous solution containing 15 wt % KOH
and 5 wt % KI. This equipment is designed to be able to dispose of one
trailer of fluorine (18 std m^3) at a flow rate of 30 slm. The KOH solu-
tion will be circulated through the spray nozzles at a maximum total flow
rate of 15 gpm (9.5 x 10^{-4} m^3/sec). The fluorinator off-gas stream will
flow cocurrent to this stream. The scrubber exit stream will pass through
a photometric analyzer for monitoring the efficiency of the scrubber.

4. OPERATING PROCEDURE

After the system has been leak tested, all salt-containing equipment
and piping will be purged with argon and heated to 600°C. All heaters
and thermocouples will be checked after the system has been held at this
temperature for several hours. MSBR fuel salt will then be charged to
the surge tank. Approximately 65 liters will overflow through the flow-
meter and circuit-breaking pot to the fluorinator. After the level is
equalized in the reduction column, the salt will fill the fluorinator to
several inches above normal operating level. The liquid-level recorders
in the fluorinator and surge tank can be checked for operability during
this operation.

Argon will be introduced to the bottom of the reduction column at
a low rate; the rate will be increased until the salt begins to circu-
late as indicated by a drop in the fluorinator liquid level, an increase
in the gas-liquid separator liquid level, and a temperature difference
across the heat flowmeter. The argon flow will be increased stepwise to
obtain data of salt flow rate vs argon flow rate. The liquid level in
the fluorinator and separator will be observed during this test. If the
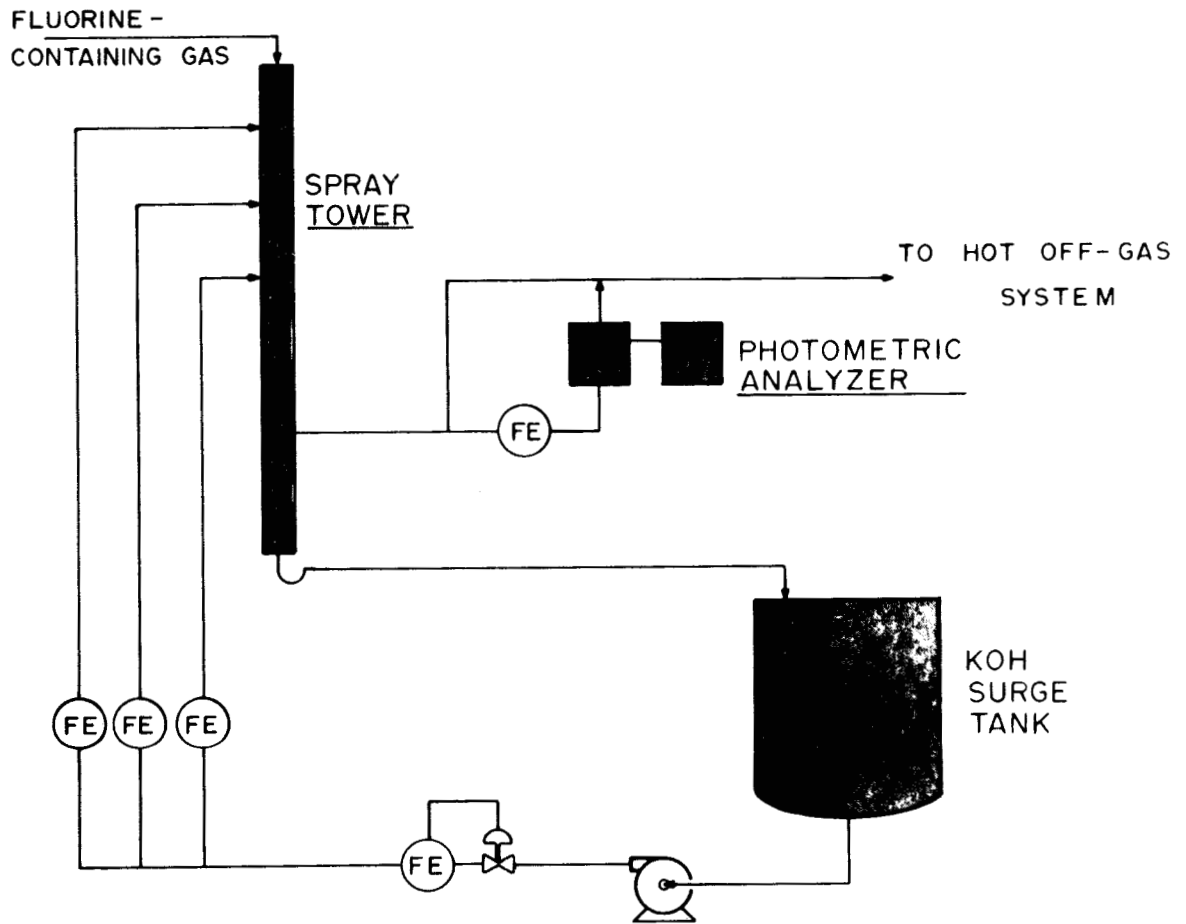
ORNL DWG. 75-15057

Fig. 5. Fluorine disposal system.

fluorinator liquid level is too high at the normal salt flow rate, some
salt will be removed to the drain tank. This can be done by thawing the
freeze valve below the surge tank, closing the system vent valve, and
opening the drain-tank vent valve to the cell. The system will be pres-
surized by the purge rotameters to transfer the required amount of salt
from the surge tank to the drain tank.

After adjusting the salt inventory, salt circulation will be started
again, and temperatures in the fluorinator will be adjusted to 530°C.
Lines and other equipment can be maintained between 530°C and 600°C.
Heat to the test section of the fluorinator will be turned off and cooling
air and water turned on. The autoresistance power will be turned on at
very low voltage (less than 1 V) and the resistance can be calculated
periodically from the current measurement as the cooling proceeds. Coolant
rates to the different zones will be adjusted to keep pipe wall tempera-
tures as uniform as possible. When all pipe wall temperatures are less
than 350°C, the resistance of the salt from the electrode to the bottom
of the fluorinator will have increased considerably. The autoresistance
power will be increased until the resistance of the salt and the wall
temperatures become steady.

Following this step, the autoresistance power will be changed, and
equilibrium resistance and temperature will be determined for a range of
powers to determine the operating range of the system. The argon flow
rate to the fluorinator gas inlet (normally the fluorine flow) will be
varied to determine the effect on operability and film thickness, as
indicated by wall temperature and salt resistance. In addition, the salt
flow rate will be varied to determine the operable range, and the sampler
will be inspected before fluorine is used.

After the system has operated reliably at various salt and argon flow
rates and the operable autoresistance power range has been ascertained,
the argon to the column will be replaced with hydrogen to determine what
effect, if any, the gas density has on the operability of the gas lift.
Argon to the fluorinator will then be replaced by fluorine. Mass flow-
meter readings taken upstream and downstream from the NaF traps will

indicate the evolution of UF_6; salt samples will be taken periodically for additional data on the fluorination reaction rate. Runs will be made at various fluorine flow rates, fluorine concentrations, and salt flow rates. After good operation has been demonstrated under different conditions, the salt film thickness will be checked by radiography. The freeze valve below the fluorinator will be thawed and salt circulation and autoresistance power stopped as soon as flow to the drain tank begins. Heat will be turned off the fluorinator and radiographs will be taken of the cooled zones.

5. MAINTENANCE

5.1 Maintenance Philosophy

Most components of the system such as the salt storage and drain tanks, separator, sampler, and traps will be designed and constructed for a long, maintenance-free service life. The fluorinator and reduction column may be replaced with equipment of alternate design depending on operating performance. All components of the system will be accessible for possible repair or replacement.

5.2 Preventive Maintenance

The operating temperature of the system will be closely controlled to prevent hot spots that could cause heater burnout. Resistance heaters are to be operated at one-half the design voltage to prolong their usage. Chemical analyses will be made of the salt (especially for NiF_2) to detect unusual corrosion. The facility will be checked regularly to detect incipient failure of parts of the system, and appropriate maintenance measures will be taken.

6. STANDARDS AND QUALITY ASSURANCE

6.1 Codes and Standards

The vessels and piping will be fabricated in accordance with the requirements specified in Sect. VIII of the ASME Boiler and Pressure Vessel

Code and Pressure Piping Code. ORNL MET material specifications and ORNL Weld Procedure Specifications will be used for construction of the vessels and piping. Because of its location at the bottom of the cell, it will be subjected to the highest pressures in the system; therefore, the design must be reviewed by the ORNL Pressure Vessel Review Committee. Details of this vessel are shown in ref. 10.

6.2 Quality Assurance

Quality level III and IV (QL-3) quality assurance standards as outlined in "Quality Assurance Program Planning for Small Research and Development Projects," QA-CT-1-109, will be applied in constructing the facility.

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