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SUBJECT: The Problem of Scrubbing the Hydrofluorination Off Gas
with Liquid HF

TO: Volatility Steering Committee

FROM: M. E. Whatley
L. E. McNeeseAbstract

Radioactive solids will be entrained by the off gas from the hydrofluorination step of the Volatility Process. The Volatility Process is being developed as a method for recovering uranium from zirconium matrix fuel elements. It is proposed to scrub these solids from the off gas in a packed bed using refluxed liquid HF. A development program has been planned and a unit designed for the experimental studies.

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1.0 SUMMARY

A development program has been planned to study the scrubbing of the hydrofluorinator off gas with liquid HF, and an experimental reflux unit has been designed.

The use of a fuel element hydrofluorination step in the Volatility Process to recover the uranium from zirconium matrix fuel elements presents the problem of removing radioactive solids in its off gas. The solids in the off-gas stream will be predominately ZrF_4 snow and fission product NbF_5 with some entrained molten salt splash. The gas will consist of a mixture of hydrogen evolved from the hydrofluorination reaction and unreacted HF.

After reviewing the possible methods for removing solids from gases, scrubbing the gas in a packed bed using refluxed HF as the liquid was selected for experimental study. Although ZrF_4 is only slightly soluble in liquid HF, the washing action of the liquid, the large area for particle impingement in the bed, and the reduction of the gas temperature through its dew point in the condenser should assure a high efficiency of solids removal. There are refrigeration requirements which complicate the use of HF reflux, but the fact that HF is already available in the system makes its use convenient.

A scouting attempt to use HF reflux in the Unit Operations' hydrofluorination facility to reduce fouling of valves in the off-gas system produced encouraging results. The unit was not, however, designed to operate over a sufficiently wide range of conditions and was not sufficiently instrumented to allow quantitative evaluation.

2.0 INTRODUCTION

A step in the proposed processing of irradiated zirconium matrix fuel elements by the Volatility Process will be dissolution of the fuel element in a bath of molten fluoride salts with an HF purge. The reaction evolves hydrogen which will be carried out with the unused HF in the off gas. These gases act as a carrier for several of the constituents of the bath exhibiting significant vapor pressures at the high temperature (500-700°C) of the melt. In addition to the volatile constituents, the violent bubbling of the melt will cause a spray, part of which will be entrained. As the off gas moves to cooler regions, the volatile components will condense out to form a dust or a smoke, which will create operational problems by fouling heat transfer surfaces, plugging valves, and contaminating the system. Further, there will be a small, but significant, loss of product uranium by this means.

The most troublesome constituents of the off gas will be ZrF_4 and NbF_5 . Rare gas fission products will be in the off gas but will cause no operational problems. The other fission product elements either will not be fluorinated to a volatile state or will be present in a relatively innocuous state. The major part of the

radioactivity in the off gas will come from Nb^{95} , about half of which seems to report to the off gas. The zirconium will be radioactive because of the presence of fission product Zr^{95} and also because of transmutation of the Zr in the original fuel elements.

The experience with the off gas from fused salt vessels has pointed up the problems. The fluorinator in the Volatility Pilot Plant was equipped with a sodium fluoride bed to act as a trap to catch the ZrF_4 and other solids (some of which are corrosion products) which would foul the system if neglected. Study of corrosion in fused salts at Battelle Memorial Institute was hampered by the plugging of off-gas lines with ZrF_4 . The bench scale hydrofluorination studies with irradiated zirconium fuel elements showed little trouble with plugging of the off-gas lines because of the low gas rates used, but the niobium activity in the off-gas lines continued to increase for the duration of the experiments.

The problem was again encountered in the engineering development phase of the hydrofluorination step. The off-gas lines were coated with ZrF_4 after every run, valves in the off-gas line were frequently fouled, and dust was carried as far as the HF recovery facility. The operational troubles in the engineering development work necessitated some tentative solution.

The first attempt to remove entrained solids was by the use of a baffled chamber; later a cooled vertical section to partially condense HF and act as a wetted wall tower was added (Fig. 1). It was made of copper and was separated from the dissolver by 6 ft of bare Inconel tubing. During operation, the cold wall was maintained at about $10^{\circ}C$ to condense and reflux the HF vapor. At low gas rates (about one lb per hour) liquid HF could flow back into the baffled chamber. The sensible heat of the incoming gas was usually sufficient to boil the liquid and keep constant liquid level so that it was seldom necessary to use the steam coil provided. At the higher gas rates it is doubtful that the liquid returned to the chamber, although there was some condensation at all gas rates used (1 to 10 lbs per hour). Since the off gas was cooled to about $150^{\circ}C$ by heat losses before it reached the baffled chamber, most of the snow had already formed, and 65% of it was deposited on the inlet pipe wall. The remainder was trapped by the condenser and collector with less than 1% escaping to the rest of the off-gas system. The device served its purpose well, but it would not be sufficiently effective for use with a radioactive system, nor did it have the instrumentation required by an adequate development tool.

In evaluating possible methods of solving the problem on a processing plant scale, the following points should be considered: (1) the dust will be radioactive, (2) its concentration will be low, (3) it will have a particle size probably in the 1-10 microns range, (4) the activity level of the HF recycle system depends upon this step. Since a high decontamination efficiency is desirable in order to facilitate the waste disposal problem and maximize the uranium recovery, it should be possible to empty the accumulated solids into the hydrofluorinator.

The methods which might be considered are gravity settling, filtration, and gas scrubbing^(1,2,3). Gravity settling is probably the simplest type of operation,

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Fig. 1. Wetted Wall Dust Collector.

requiring only a chamber in which the gas velocity is reduced sufficiently to enable particles to settle out. When the particles are smaller than about 50 microns in diameter, however, very low velocities are required. The terminal settling velocity for a one micron particle is about 10^{-4} ft/sec, and for a 10 micron particle is about 10^{-2} ft/sec. These vary, of course, with the viscosity and density of the medium and with the density of the particle.

The separation of a dust from a gas by filtration^(4,5) is more complex than one would immediately suppose since the pores in the filter media are usually many times the particle size. The dust-laden gas must build up a precoat on the filter before the separation efficiency is satisfactory. This depends primarily upon the processes of impingement on, settling on, and Brownian movement to the media. Where the particle size and concentration are low, it is difficult to form this necessary precoat. Consideration should also be given to the problem of changing contaminated filter media.

Dust removal by scrubbing a gas with a liquid has been shown effective in many applications, especially for particle sizes in the range 1 to 10 microns and larger.^(6,7) This operation is thought to be most applicable to the hydrofluorinator off-gas problem. The gas from the hydrofluorinator would be scrubbed with liquid anhydrous HF in a packed bed, the liquid HF being obtained by condensation out of the off-gas stream if possible.

It is intended to discuss below the significant characteristics of the hydrofluorinator off-gas stream, the anticipated problems in the design and operation of a gas scrubber using liquid anhydrous HF, and the outline of an engineering development program to study these problems.

3.0 CHARACTERISTICS OF THE HYDROFLUORINATOR OFF GAS

The principal constituents of the off gas will be the hydrogen evolved from the dissolution reaction:

and the unused HF. The per cent utilization of the HF has not been established. It possibly could attain a maximum of eighty or ninety per cent, but maximum values of about sixty per cent are more probable. At the end of the dissolution the utilization will tail off to zero. This means that the HF content on a formal basis is expected to range from 57 to 100% HF. The other constituents are of much lower vapor pressure and will be carried by the HF and H_2 .

The solids in the off gas are principally ZrF_4 and the physical behavior of the dust will depend upon the behavior of ZrF_4 . The vapor pressure of pure ZrF_4 at room temperature is vanishingly small, but⁴ is 1 mm at 650°C and 760 mm at 902°C (Fig. 2).

Its vapor pressure above the molten salt will be dependent upon its concentration

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Fig. 2. Vapor Pressure ZrF_4 .

in the salt melt, which can range from zero to 58 mol per cent. For lack of better information, it can be assumed that Raoult's law holds. At an operating temperature of 650°C, then, the gas would contain about .05 mol per cent ZrF_4 , which would condense rapidly as the gas temperature was lowered. These conditions are ideal for the formation of very small particles. Where the gas passes cold surfaces there would be deposition of snow. In small operations, the deposition of snow on container walls in the 300 to 500°C temperature range has been found to account for a sizable fraction of the ZrF_4 volatilized. There has always been some entrainment of dust, and this seems to increase as the gas rate increases and as the ratio of vessel volume to surface increases. The entrained particles are thought to be in the range of 1 to 10 microns in diameter and gradually deposit themselves throughout the off-gas system.

Of equal importance with zirconium in the solids is the radioactive niobium. Since it is present only as a fission product, its concentration depends upon the history of the fuel. Using reasonable assumptions for burnup, fuel element history, and dissolution conditions, and assuming that all Nb reports to the off gas, the niobium concentration in the off gas would be less than 0.01%. It probably will be lower than this by orders of magnitude.

The niobium in the off gas will be in the form of NbF_5 , which is very volatile (Fig. 3). Experiments with irradiated fuels show that only about half of the niobium is fluorinated to this state, and the remainder stays in the salt. It has further been observed that the niobium is deposited from the gas onto the pipe walls. The mechanism for the deposition might be either the reduction of the fluoride by hydrogen or metal walls, or the absorption of the NbF_5 by the ZrF_4 , possibly with the formation of an intermolecular compound. The high vapor pressure of NbF_5 , the similarity of NbF_5 to ZrF_4 , and the inevitable presence of ZrF_4 particles render improbable the independent nucleation of NbF_5 particles.

The rare gas fission products will, of course, report to the off gas, but they will pass on through the system as noncondensibles and will cause little operational difficulty. The iodine fission product will report to the off gas as HI, but in the presence of HF will form no stable compounds. Being much more volatile than HF, the HI will probably distill nicely from it in the HF recovery system and leave with the noncondensibles. Other volatile fission products like TaF_6 , MoF_6 , and RuF_5 are not expected under the reducing conditions of the dissolution.

4.0 DUST REMOVAL BY SCRUBBING A GAS WITH A LIQUID

The mechanisms by which a liquid serves to remove a dust from a gas may be summarized as follows:

1. Impingement. When a dust-laden gas sweeps by liquid drops or a liquid film, impingement of particles on the liquid will occur. This action is usually limited to removal of particles whose size is ≥ 5 micron since the smaller particles lack the inertia required for impingement.

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ORNL-LR-DWG 30902 Fig. 3. Vapor Pressure of NbF_5 .

2. Diffusion. Dust particles interdispersed among liquid droplets in a gas stream will be deposited on the liquid drops by Brownian diffusion or motion. This mechanism will be predominant in the collection of submicron particles and may be appreciable for dust particles in the range up to 5 micron diameter. Diffusion as a result of fluid turbulence may also be a significant factor in dust deposition.
3. Humidification. The humidification of a gas by the introduction of a liquid spray may alter the electrostatic surface forces on the suspended dust particles, causing them to flocculate. The larger flocs may then be separated out more readily by other means such as settling or impingement.
4. Condensation. If the temperature of a gas is lowered causing the gas to pass through its dew point, condensation will occur with the dust particles, particularly the smaller ones, acting as condensation nuclei. This increases the effective size of the particles and simplifies subsequent collection.
5. Wetting. Contrary to prevalent beliefs, the wetting characteristics of the liquid do not play a major role in the actual process of dust collection. In general, improvements in collection efficiency resulting from the use of wetting agents are small.
6. Surface Washing. Often the liquid is not dispersed in the gas but flows as a film over the collecting surfaces. The action of the liquid in such a case is that of washing the collecting surface free of dust and avoiding re-entrainment.

The best physical method of effecting gas-liquid contact depends upon the nature of the phases and the relative convenience of the alternatives. A packed bed is attractive for low dust concentrations where plugging is not a problem. For the hydrofluorinator off gas, a packed bed has the advantage of avoiding spray nozzles for liquid HF with the required associated pumps, and offers a relatively low pressure drop (0.5 to 1.0 in H_2O /ft) through the bed. It is expected to provide adequate surface for impingement and diffusion particle collection.

5.0 THE DEVELOPMENT OF A DISSOLVER OFF-GAS SCRUBBER USING REFLUXED ANHYDROUS HF

The unit operation of scrubbing a gas with a liquid in a packed bed is fairly common, and the conventional correlations of flooding velocities are expected to be valid. The height of tower necessary to effect sufficient removal is not amenable to analytical treatment; however, this can be easily determined by well planned experiments. The most formidable aspect of this operation is effecting controlled reflux of the HF. This problem is complicated by the peculiar polymerization characteristics of HF and its relatively high volatility. Ideally, a reflux condenser, placed above the packed bed, is adjusted so that the rate of uncondensed HF allowed to pass through the condenser is exactly equal to the rate

of HF being carried into the bed with the off gas from the reactor. The problems involved in this are best appreciated by considering the properties of HF.

5.1 Physical Properties of Hydrogen Fluoride

At low temperatures and atmospheric pressure, hydrogen fluoride can associate to the $(\text{HF})_5$ form. At 20°C it is still of a form $(\text{HF})_3$ and does not completely dissociate until temperatures as high as 60 to 70°C are reached. This association is, of course, a function of pressure. The association releases about 6.7 kilocalories per gram formula weight of HF.

As a result of the high heat of association, the latent heat of evaporation is decreased. This makes it difficult to control the vapor rate by controlling the heat input to the reboiler or the heat removal from the condenser. Because the HF is highly associated at the exit gas temperature, relatively large amounts of HF can be carried off though the vapor pressure of HF may be small.

The freezing point of HF is -83°C . At atmospheric pressure, it boils at 19.5°C , and its critical temperature is 230.2°C . The vapor pressure curve is shown in Fig. 4. If the packed bed is to operate at a constant liquid inventory, the exit gas from the reflux condenser must have the same composition as the inlet gas to the bed. This means that the cooling surface in the condenser must be of a temperature less than the dew point of the dissolver off gas. Because the association of HF is dependent upon temperature, the dew point is unusually sensitive to gas composition (Fig. 5). This is directly related to the HF utilization in the dissolver or the amount of hydrogen that is produced. The dew point becomes quite low and, for the high utilizations, approaches the boiling point of hydrogen (-252.7°C). At utilizations greater than 60 to 70%, addition of hydrogen fluoride to the scrubber will be necessary owing to the very low temperatures required to reach the dew point.

Other problems in the use of liquid HF for scrubbing the off gas have to do with the compatibility of HF with the entrained solids. The solubility of zirconium tetrachloride in liquid hydrogen fluoride follows an inverse relationship to temperature (Fig. 6). Extrapolation of the existing data shows a solubility of 7.6×10^{-3} grams of ZrF_4 per 100 grams of hydrogen fluoride at the boiling point of HF. There are no quantitative data available for the solubility of niobium pentafluoride in HF. Similarly, there are no quantitative data on wettability of zirconium tetrafluoride or niobium pentafluoride particles with HF. But the degree of wetting is greatest between materials of similar molecular structure; therefore, one would expect zirconium tetrafluoride and niobium pentafluoride to be wetted by liquid HF.

Condensed solids found on pipe walls after hydrofluorination tests have a low bulk density and show little adherence to the walls. It is probable that these solids can be washed from the walls into the hydrofluorinator by liquid HF. Limited experience with the unit installed on the Unit Operations hydrofluorinator has been encouraging.

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Fig. 4. Vapor Pressure HF.

Fig. 5. Off-Gas Dew Point vs. HF Utilization.

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Fig. 6. Solubility of ZrF_4 in Liquid HF .

For corrosion purposes it is very desirable to minimize the water content in the reflux hydrofluoric acid. Commercial anhydrous hydrochloric acid may contain as much as one per cent water by weight. This water will certainly accumulate in the reflux system. Vapor containing less than 1% water is in equilibrium with from 10-15 weight % water in the liquid phase. It will be necessary either to ascertain that no large amount of water can reach the reflux unit or to make provisions for an occasional purge to remove the accumulated water.

6.0 PROPOSED SCRUBBER DESIGN

The design of the scrubber system to be tested includes a condenser, a packed scrub section, and a reflux vaporizer (Fig. 7). The temperature of the dissolver off gas will be lowered from approximately 450 to 50°C by process cooling water in coils provided at the lower end of the inclined section. The heat removal rate will be adjusted so that the gas will contain sufficient heat to vaporize the liquid HF reflux which has passed through the packed bed.

In the bed, the larger particles will be removed by impingement upon the wet surfaces of the packing. Upon reaching the condenser, the gas will pass through its dew point and condensation will occur both on the condenser surfaces and on the small dust particles present in the gas. During condensation, the effective particle sizes will become larger so that impingement on the condenser surface or gravity settling will effect their removal. It is important to note that during condensation the greatest gas velocity will be in the direction of the condenser surface.

A predetermined fraction of the gas stream will be condensed to serve as reflux for the packed bed. The flowing liquid will remove particles from the condenser surface and the packed bed and carry them down the column to be deposited in the inclined section at the point of HF vaporization. The rate of heat removal in the condenser will be relatively small; ignoring the sensible heat involved (approximately 2%) the refrigeration load will be the product of the heat of vaporization of HF (176 Btu/lb) and the liquid reflux rate.

The reflux rate must effect solids removal without flooding the packing. This rate is a function of the rate of heat withdrawal in the condenser and of the system inventory. Since the inventory is a function of condenser temperature, the reflux rate can be controlled by the rate of heat withdrawal and the temperature at which it occurs.

Intermittant return of liquid HF to the dissolver will be prevented by maintaining temperature $T_1 > 19.5^\circ\text{C}$. The flow of cooling water will be such that temperature $T_2 \approx 19.5^\circ\text{C}$. When the HF utilization is $> 60\%$, makeup HF will be added to the system since the required condenser temperature would be less than a practical value. Since the dew point at this utilization is -17.5°C , a condenser temperature of approximately -30°C would be required.

After dissolution and salt transfer have been completed, the dissolver

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Fig. 7. Liquid HF Reflux Gas Scrubber.

temperature will be lowered to approximately 40°C to allow the liquid HF to return to the dissolver to be vaporized. Through the effects of solubility and washing, the solids should be carried into the dissolver.

7.0 MATERIALS OF CONSTRUCTION

The scrubber system will be subjected to corrosive conditions such as flowing liquid HF and HF concentrations of 80-100% by weight. In general, the choice of a metal is based upon the temperature to which the HF is to be raised, whether the HF will be in the liquid or vapor phase, and the extent to which flow conditions exist at the metal-acid interface. With the exception of the noble metals and silver, all metals which have been found satisfactory for containing anhydrous HF owe this property to the formation of a protective fluoride film on the metal wall. The effect of process conditions upon this film determines the suitability of the metal for its intended application.

Metals in which the rate of diffusion of HF through the protective fluoride film increases markedly with a rise in temperature are said to be "temperature sensitive". Metals in which the flow of liquid HF over the surface causes the protective film to flake off rapidly are termed "velocity sensitive". The following metals are among those found satisfactory for handling liquid HF:

1. Carbon Steel. Although somewhat temperature sensitive, it is not velocity sensitive, and may be used for pump impellers, pipe lines, and valves. It is adequate for pressure vessels up to a temperature of 75°C.
2. Monel. Monel has been found the most generally satisfactory of the metals considered economically practical. The corrosion rate at elevated temperatures and under drastic flow conditions is small.
3. Copper. Copper forms a protective film in the presence of HF and is satisfactory for handling it in the vapor phase at temperatures up to 400°C. The metal is velocity sensitive, however, and streams of liquid HF cause considerable corrosion.

The scrubber system, including the packing, will be made of Monel. It is felt that copper will be satisfactory for the condenser despite the small quantity of flowing liquid HF. A Lapp pump having Monel pumping parts will be employed. A carbon steel surge tank will also be used.

8.0 PROPOSED EXPERIMENTAL STUDIES

Two scrubber systems have been designed and will be constructed for testing with other Unit Operations dissolution studies. One system will be used in conjunction with an existing dissolver system; the second with a system for study of dissolution in the absence of molten salt. A discussion of the second system may be found in CF-58-5-44.

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