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SUBJECT OR TITLE

Chlorine Triflouride Process

TO

O.F. Hill

FROM

C. Groot

[redacted]

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TO: Dr. O. F. Hill

DATE: February 5, 1952

FROM: Dr. C. Groot C Groot

CHLORINE TRIFLUORIDE PROCESS

The uranium in irradiated Hanford slugs is eventually to be converted into UF_6, the process material for the K-25 Gaseous Diffusion Plant. UF_6 is easily and effectively purified by distillation. Hence if the hot slugs could be fluorinated directly, and the fluoride purified, this might provide a much simpler process, with lower chemical and waste disposal costs, than the present system of converting the uranium to the nitrate, purifying the nitrate, and going through UO_3, UO_2, and UF_4 to get to the desired product UF_6.

The uranium slugs may be fluorinated either with fluorine, bromine trifluoride, or chlorine trifluoride. Fluorination with fluorine is a gas phase reaction, and the heat transfer problems have not been solved. Fluorination with chlorine or bromine trifluoride is liquid phase reaction, with much simplified heat transfer problems. This report deals with the chlorine trifluoride process.

The process consists of dissolving the irradiated uranium in ClF_3-HF mixture, which converts the uranium to UF_6, the plutonium to PuF_3, and the fission products to fluorides of their highest valence state. The ClF_3 is converted to ClF, a gas under the reaction conditions, from which CF_3 is regenerated by adding F_2 and passing the mixture over copper at 300°C.

The solution is distilled through a gas filter into a distillation system. The PuF_3 and the non-volatile fission product fluorides are left behind. The material transferred is then rigorously distilled. The tops consist of ClF, HF, ClF_3, and TeF_6 and some UF_6. The product is UF_6. The bottoms include UF_6, RuF_5, and other fission products.

The plutonium is recovered by washing out the reactor pot with aluminum nitrate, which dissolves the PuF_3 and most of the fission product fluorides. This solution is then ready for solvent extraction, for which a T.T.A. system seems peculiarly suited.

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OBJECTIVE

The objects of this report are to evaluate the chlorine trifluoride process, in terms of chemical feasibility, economy, and development status.

SUMMARY AND CONCLUSIONS

The process has been demonstrated to be chemically feasible. A great deal of development work is necessary to demonstrate that it is safe and economical. Some of this work is underway.

DISCUSSION

A. Dissolution

The dissolution step has remarkable potentialities, in that the uranium is converted directly to the desired volatile UF_6, while the plutonium remains as PuF_3. While the chlorine trifluoride is the fluorination agent, this is continuously regenerated by the addition of more fluorine so the net reaction is

$$U + 3F_2 \xrightarrow[HF]{ClF_3} UF_6$$

Thus with fluorine at $0.80/lb., the material cost is only $0.40/lb. uranium, assuming 96% utilization of F_2. There are no gaseous by-products and no great volume of water to be removed later. The process has many of the advantages (and many of the problems) of fumeless dissolving. As in any proposed dissolving procedure, we would have the current costs of material and waste disposal from the jacket removal step. However, the dissolving as currently practiced (room temperature; 40 psig.) uses an excessively long time cycle. Since the size of the dissolver is limited by critical mass considerations, all the potential savings in operating costs will be lost in the excessive capital cost of a multitude of dissolvers unless this time cycle is improved. The dissolver cycle would consist of loading, jacket removal, drying the dissolver by evacuation and ClF_3 gas, introduction of the bulk of the ClF_3-HF mixture, reaction, vapor transfer of volatiles, dissolution of PuF_3 and washing. The loading presents no new difficulties, except that since the reactor will operate from vacuum to at least 60 psi. (perhaps much higher), the reactor will have to be a pressure vessel with a very good closure. The leak-tight closure of the charging hatch will be a difficult job. The present jacket removal technique should be adequate. Drying the dissolver will be a slow and tedious job. It must be done thoroughly as ClF_3 and F_2 react explosively with water. A combination of heating and evacuation will be required. When most of the water is gone, the rest can be removed with cautious addition of ClF_3 vapor.

The charging of the ClF_3 is another step that will need study. The ClF_3 is currently charged as the vapor, and condensed in the reactor. This is a slow job, requiring a lot of refrigeration, and will be even worse on a

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large scale with a lower surface to volume ratio. It will be necessary to develop a technique for adding liquid ClF_3. This at best would be merely life tests on existing valves designed for gaseous fluorine service, but it might develop in valve and closure design problems.

The dissolution reaction itself is unsatisfactory because of slow rate. The use of ClF_3 alone results in an extremely slow rate. The use of ClF_3-HF mixtures results in much more rapid attack on the slugs, and also on the reactor. By use of a high mole ratio of HF to ClF_3 (3.6:1) a slug could be dissolved in five days, but this high ratio of HF to ClF_3 results in a HF-UF_6 azeotrope. This azeotrope may be broken, but this has yet to be proved. Use of a low (0.56:1) mole ratio HF to ClF_3 results in much lower dissolution rates, in fact one slug only half dissolved, and then ceased to react. By slicing slugs into 1/4" slices the reaction goes to completion with 0.44:1::HF:ClF_3 in about 3-4 days @ 20°C. and 50 psig.

It is well realized at K-25 that this low reaction rate is unsatisfactory, and that the HF complicates the separation problem and increases the corrosion rate. Studies are now underway on effect of temperature and pressure on reaction rate, and the possible catalytic effect of the group V elements. It is noted that irradiated material reacts five times as fast as virgin uranium; this at once provides a clue to how rates might be raised and complicates the interpretation of cold rate studies. The reaction is much faster along the axis of a slug than radially.

The reaction produces ClF as a by-product. This is continuously converted to ClF_3 by addition of F_2 and passing over hot copper turnings. This reaction seems reasonable although the fission products may be poisoning the catalyst. A catalyst of 4.3 cubic inch volume converts the ClF from 200-1000 g/day uranium dissolution.

It is very important that the converter be large enough, as the system becomes unstable if the converter is too small. The reactions are

$$(1)\quad U + \underset{\text{(liquid)}}{3ClF_3} \longrightarrow UF_6 + \underset{\text{(gas)}}{3ClF}$$

$$(2)\quad 3F_2\ \text{(gas)} + \underset{\text{(gas)}}{3ClF} \longrightarrow 3ClF_3\ \text{(liquid)}$$

If reaction (1) goes faster than reaction (2), the pressure in the system may rise above the available fluorine pressure and it becomes necessary to bleed the system to reduce pressure, to permit the introduction of more F_2. The converter in the K-25 Pilot Plant is too small to handle the initial rate of reaction.

After the reaction is completed, the volatile components are removed by vapor transfer. This presents another scale-up problem, in that the rate of such transfer is proportional to the surface, not the volume, of the transferring vessels. Current practice is to bleed off the F_2 and ClF to the stack, distill the bulk of the ClF_3 and HF to a separate tank for reuse, and then distill the rest of the volatiles to a still pot. This transfer is through a nickel barrier backing filter, which is more than usually effective. The Pu exists as non-volatile PuF_3, and is left behind.

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This uranium-plutonium separation raises a critical mass problem. As long as the plutonium is associated with a large amount of U-238, the reactor cannot go critical. Once this U-238 has been removed as UF_6, and particularly in the plutonium dissolution step, critical mass control becomes very important. For this reason, the charge to a reactor may not exceed 325 g. of plutonium, even though this might be contained in as little as one half ton uranium. It is this limit on charge size that makes the reactor time cycle so critical. The basic unit is the half ton reactor, and the plant must have as many of these as the production requirements and time cycle dictate. Table I shows the number of reactors required for a 2-1/2 ton plant at various time cycles (including plutonium removal) and my estimate of the probability that these time cycles will be equaled or bettered. It may be seen that the process must be much improved to become economically feasible.

TABLE I

Time Cycle, days	Reactors at 2-1/2 tons/day	Probability of Success at this time cycle
30	150	0.99
15	75	0.9
5	25	0.7
2	10	0.4
1	5	0.2
1/2	3	0.1

In this table, an allowance of 30% down time is included in the time cycle.

B. Distillation

The distillation step is difficult, but very effective. The difficulty arises from the high freezing point of UF_6 (64°C.). Hence the whole column, including the stillhead, must be maintained at 70°C. To maintain a suitable temperature differential to condense ClF_3 in the stillhead means a pressure of 125-150 psig. in the stillhead, and 130-140°C. in the pot. At this temperature and with this highly corrosive mixture a leak becomes likely, and a large loss of UF_6 and serious spread of contamination would result from even a small leak. Most of the fission products and plutonium would have been removed by this time, but even so, if the still blew up, it would make a pretty large building uninhabitable for some time.

This difficulty is avoided in the pilot plant by operating a batch still in three phases. These are

A. Cold phase.

The UF_6 is retained frozen in the pot, and the ClF_3 is distilled off with a cold condenser to provide reflux.

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B. Transition.

The apparatus, including condenser, is heated above the freezing point of UF_6, and the remaining ClF_3 taken off as gas.

C. Hot phase.

The whole unit is filled with refluxing UF_6.

This technique is an interesting and ingenious way of making the plant work, and completely removes the ClF_3 from the UF_6. However, since there is no reflux during the transition phase, just when reflux is most needed, there is a considerable loss of UF_6 to the light ends. It is thus necessary to recycle these, along with the light fission products. While this technique makes it possible to use the pilot plant, it does not give nearly the separation possible or desirable.

The distillation to remove high boiling fission products is much more satisfactory. The column operates at essentially the same temperature top and bottom, with only such temperature differences as required to give heat and material transfer. The ~~following~~ operation runs at about 1200 mm. (ca 12 psig.). There is considerable loss to still bottoms because of column holdup. This would be largely eliminated in a production unit, which would employ a continuous still.

The one slug-scale run made so far made specification product, namely

5% of natural uranium β.
21% of natural uranium γ.
6 parts plutonium per billion parts uranium.

This run was made at 50-1 reflux to product, which is more than necessary.

Overall material balance was 67%, and 36% of the material charged was in the product receiver. On a continuous basis, one should not lose more than 1% to the heads and 4% to the tails, and 99% recovery seems possible.

C. Plutonium Recovery

Little work has been done on the plutonium recovery problem. Since manpower for this project is extremely limited, emphasis was placed on merely recovering the plutonium and fission products from the reactor in a form that can be used in a solvent extraction process.

It has long been known that $Al(NO_3)_3$ is a good salting agent for plutonium, and it was shown that Versene did not inhibit the extraction of plutonium at low pH (ca 0.5).

The recovered solutions of plutonium and fission products from the pilot plant runs are being retained for a later development of the process either by K-25 or, perhaps, a laboratory more experienced in solvent extraction work than K-25.

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The plutonium in the reactor is in the form of PuF_3. It could conceivably be removed by more drastic fluorination as PuF_6, but it is hard to see how the uranium specifications could be met if this were done. Almost certainly some of the PuF_6 would get in the UF_6. Since the reactor is going to be used in an aqueous cycle anyway on jacket removal, it would be better to evacuate the reactor, and steam it out carefully (there is danger of a minor explosion here), and remove the Pu as an aqueous solution.

The plutonium can be largely removed by two washes with 5% $Al(NO)_3$ (computed as such, not the hydrate). As operated so far, the two washes were the full volume of the reactor, so the Pu in the product stream was only 0.15 g./l. or of the same order as UAF. Hence the Pu recovery will be almost as expensive as in Purex, since the same volume of solution will have to be handled, and probably also through two cycles. The time cycle of 96 hours for the Pu removal is much too long. It cannot be decreased by raising the temperature because of corrosion difficulties. There is some hope of removing the plutonium in Versene at pH 7, which would not be corrosive, but no work has been done on this that considered the importance of the time cycle. The plutonium could be recovered from the Versene solution by solvent extraction.

The low concentration of plutonium in these solutions does not arise from low solubility, but rather from the difficulty of working out a large reactor with a small amount of solution. In other words, the volume of solution used is not determined by the volume needed to dissolve the PuF_3, but rather by the volume needed to wash the space where the uranium used to be. If some more efficient technique, say a spray wash system, could be made to work, the volumes of plutonium solution to be handled might be cut by a factor of 10.

STATUS AND FUTURE DEVELOPMENTS

The present status of the process is that it is emerging from the research stage into the development stage. It is one of the most promising alternative to carrier precipitation or solvent extraction for the separation of uranium, plutonium, and fission products. It is certainly the most direct, and probably the most effective way of making pure UF_6 from irradiated metal.

The process is, however, a long way from demonstration as a safe and economical process. A good deal of excellent work has been done on the process, but even more must be done than has been done. This work will be slow and difficult; it would be hard to imagine more difficult materials to work with than plutonium, fission products, and fluorine.

The best that could be hoped for in future developments would be as follows:

1952 - Laboratory and pilot plants studies, hopefully leading to the clearing of all the difficulties mentioned in this report.

1953 - Semi-works testing, including cold tests on full scale equipment.

1954 - Scoping and selling process, clearing up minor points, accurate cost studies.

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January 1955 - Decision to build a production plant.

January 1956 - Break ground.

January 1958 - Plant on stream.

The staff now working on this project might at best solve the problems of the uranium steps by the end of the year. If they also have to work out the plutonium cycle, another year will be lost, for they will not even start on this until 1953, and will lose considerable time getting set up for and used to plutonium work. If the plutonium cycle could be worked over simultaneously, say at O.R.N.L., a year might be saved.

The above estimates are guesses as to what might be the schedule, if the process works out. To estimate the chances of this process working out is very difficult, almost guess work. My own opinion is that there is one chance in three that the process will develop into something more economical than solvent extraction, and one chance in ten that it will be enough more economical to shut down a solvent extraction plant.

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