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NYO-1467

CLOSING RESEARCH REPORT

DECEMBER 31, 1951

BY

J. T. PINKSTON AND KARL S. WILLSON

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For The Atomic Energy Commission

H. B. Canell
Chief, Declassification Branch

THE HARSHAW CHEMICAL COMPANY
CLEVELAND, OHIO

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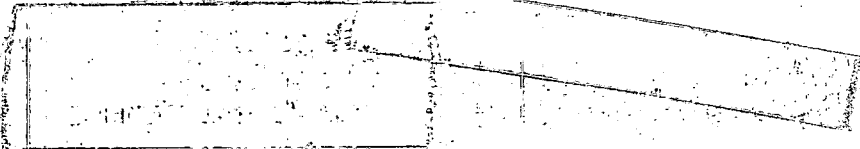
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ABSTRACT

This report summarizes briefly the work done on various projects by the Research and Development Group of Plant C of The Harshaw Chemical Company during its existence from September 15, 1950 until December 31, 1951. References are given to various reports covering in greater detail the results secured by the group.

The major accomplishment has been the development and plant scale installation of a process for uranium refining using mixer-settler equipment and a TBP-kerosene mixture as the solvent for the countercurrent extraction of uranyl nitrate from raw slurries.

Various other projects have been studied briefly.

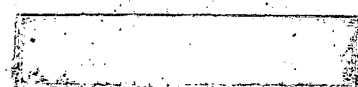
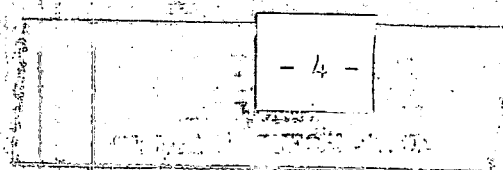


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I. PURPOSE AND PROJECTS OF THE RESEARCH GROUP AT HARSHAW PLANT "C"

When the Research and Development Group was activated on September 15, 1950 at Plant C of The Harshaw Chemical Company, its major responsibility was to develop an improvement over the then operating process for production of uranium dioxide. During its existence, the Group was also called upon to consider briefly several other problems of importance to the Atomic Energy Commission.

1. Production of Uranyl Nitrate Solutions

Production of a concentrated solution of uranyl nitrate is the first step in production of uranium dioxide from various uranium feed materials received at Harshaw. In the process operating at the time the Research Group was established, the feed material was digested with nitric acid to give a neutral slurry; the slurry was filtered and the filtrate then contacted with diethyl ether into which the bulk of the uranyl nitrate was transferred in a single batch extraction. The ether solution, after washing to remove impurities, was stripped with water to give a solution of uranyl nitrate.

Press cake from the filtration operation was repulped, refiltered and again extracted one or more times with ether. The final press cake still contained uranium values and was shipped away for further reworking.

The extraction scrubbing and stripping operations involving the ether were done in a single unit which was operated batchwise without adequate means of clean separations between operations.

(It should be noted at this point that the operations were carried out in equipment, and by methods, inherited from other producers who brought about their developments under extreme wartime pressure).

At the very outset of the Research program, it became apparent that a continuous process with elimination of filtration and reworking of solutions was most desirable and might be expected to lead to production of a better product at a lower cost. Elimination of ether and replacement by a less hazardous, more selective solvent was also indicated.

2. Denitration of Uranyl Nitrate Hexahydrate to Uranium Trioxide

Following buildown of the dilute uranyl nitrate solution (secured by extraction as described above) to uranyl nitrate hexahydrate, this latter material is denitrated by further heating in pots equipped with sweep agitators. The resulting uranium trioxide has in general been satisfactory for further processing but because of dust problems in emptying the pots, and also because of the desirability of a continuous process capable of greater capacity, some study of other procedures appeared desirable.

3. Reduction of Uranyl Trioxide to Dioxide

Reduction of the trioxide by hydrogen ("cracked" ammonia gases) in heated Rockwell furnaces ordinarily gave a dioxide suitable for further processing. However, occasional unsatisfactory product indicated the need for study of the matter of "Reactivity". Earlier studies had indicated the lack of reactivity might be due to variations in the trioxide, to poor reduction technique or to variable operation in the subsequent hydrofluorination step for production of uranium tetrafluoride.

Because of the numerous variables, a study of basic factors appeared urgent prior to any attempt to modify plant techniques.

4. Reduction of Uranium Hexafluoride to Tetrafluoride, and Attempted Production of a Dense Tetrafluoride

Because of the potentially great amounts of by-product hexafluoride available, and the desirability of reducing this material to a dense tetrafluoride suitable for metal production, the Research Group was asked to study this problem. Only a few exploratory tests could be run, however, before pressure of work on the TBP project necessitated dropping of this project.

5. Production of Uranium Metal by Reduction of Various Compounds

Availability of uranium materials other than dense tetrafluoride suggested the desirability of direct reduction of these compounds to metal by means other than the bomb technique. Time permitted

only a few exploratory tests before the project was abandoned.

6. Electrolytic Production of Uranium

Earlier tests by other groups had indicated the possibility of securing uranium metal by electrolysis in anhydrous melts. Again, only exploratory tests were made before the group was inactivated.

7. Recovery of Uranium Values from C-Liner Materials

Recovery of uranium values from C-Liner materials according to proposed methods involved considerable expense due to the neutralization of large amounts of alkaline earths. Use of a selective solvent for uranium values or other means of avoiding use of large quantities of acid appeared worthy of study and some tests were carried out.



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II. RESULTS AND CONCLUSIONS

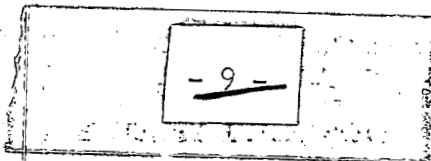
The work of the Research Group has been covered in a series of Progress and other Reports bearing the numbers NYO-1452-1466 inclusive. The following reviews give more specific references to some of the projects but for the Tributyl Phosphate (TBP) extraction process in particular, all reports should be consulted for continuity in the development of the project.

1. Production of Uranyl Nitrate Solutions

As mentioned earlier, first evaluation of the ether-batch extraction process indicated the desirability of developing a continuous process which would involve a less hazardous solvent. Also, the use of equipment to provide the necessary extraction stages to effect essentially complete removal of uranium values without filtration or reworking of slurries appeared most desirable.

TBP-kerosene solvent, according to available data, appeared promising and lab scale tests followed by semi-pilot plant scale operations confirmed the value of this solvent, both with regard to ease and safety of operation and purity of product (see NYO-1456).

A full scale plant (see NYO-1456, 1460 especially), to serve as its own pilot plant, with consequent saving in time and money was designed on the basis of relatively meager tests. This plant was



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installed and put into operation on September 4, 1951 immediately after stopping of the older process.

The new process, in spite of expected delays during conversion of equipment from the old process and adjustment of instrumentation, has produced from the start materials of high quality and, after the first two months, in quantities approaching the design capacity of the plant.

Operation of the plant is largely as projected except for some relatively minor changes involving handling of the stripped solvent (see NYO-1462 et seq.).

Except for floor drainings due to leakage, spillage, etc., little reworking of materials is necessary. After somewhat variable results during the start-up period, spent raffinate has consistently contained 0.01 g Uranium per liter or less.

2. Denitration of Uranyl Nitrate Hexahydrate to Uranium Trioxide.

Desirability of a continuous denitration process to minimize dust problems indicated possible use of an enclosed rotating drum with either internal or external heating, or both. External heating appeared preferable since heat applied to the drum might result in corrosion of the drum with consequent contamination of the product.

A small "flaker" unit (NYO-1453) was operated in the laboratory, with the rotating drum first picking up a layer of molten

uranyl nitrate (at about 190-200°C), then passing under radiant heating coils. The resulting uranium trioxide, in a flake-powder film, was removed from the drum by a doctor knife.

The product was found to be well denitrated although still containing somewhat more volatiles than the usual UO_3 produced in the denitrating pots. The bulk density of the oxide was somewhat lower than desired for conversion to UF_4 for metal production.

Results were sufficiently promising, however, that a large unit, capable of producing 30#/hr. was set up by adapting a vacuum filter. In this unit, heat was supplied by radiant gas-fired stainless steel tubes (NYO-1457,1461). This unit essentially confirmed the findings of the smaller unit in that while a well denitrated material could be formed the bulk density was too low to permit use of the material in current operations for metal. It appeared to be ideal, however, for conversion to UF_6 , for both the reduction to UO_2 and the hydrofluorination to UF_4 proceeded very readily.

3. Reduction of Uranyl Trioxide to Dioxide

The occasional difficulty in reducing trioxide to UO_2 or in the subsequent hydrofluorination step indicated the desirability of a laboratory scale test unit for investigating the factors involved. Such a unit was constructed and some tests made which indicate type of

crystal structure, size of particles and other characteristics may play a part in this situation. A rather detailed review of the problem and the work done is covered by NYO-1466.

4. Reduction of Uranium Hexafluoride to Tetrafluoride, and Attempted Production of a Dense Tetrafluoride

Reduction of hexafluoride was studied using a variety of organic liquids. Reduction occurred readily in many instances, with perchloro-ethylene giving the best results (NYO-1457). A high assay green salt (UF_4) was secured but in all the tests, this compound had a low bulk density which is unsuitable for production of uranium metal by current procedures.

Attempts to find means of securing a denser product by use of a solvent, by various mechanical means, or variable means of contact of the hexafluoride and reducing agent were unsuccessful (NYO-1457, 1458).

5. Production of Uranium Metal by Reduction of Various Compounds

Uranium metal was produced in small scale tests by feeding the uranium compound (UF_6 , UF_4 , UO_3 , or UO_2) into a graphite crucible containing magnesium, heated by an induction furnace to 1000° or $1500^\circ C$. (NYO-1462). A fine to coarse uranium powder was secured and the process appeared worthy of further study.

6. Electrolytic Production of Uranium Metal

Exploratory tests were made, largely paralleling earlier

work by others, using fluoride melts contained in a graphite crucible shielded on the outside by a stainless steel cup and heated by a gas burner. Some uranium metal in granule form was secured (NYO-1457-1458).

7. Recovery of Uranium Values from C-Liner Materials.

These materials, reportedly containing up to 2% uranium as metal, oxides or fluoride, were scheduled to be handled by digesting the mass of material in acid followed by a precipitation and recovery procedure. The desirability of finding a solvent which would selectively remove the uranium values without dissolving the alkaline earth materials comprising the bulk of the material was apparent. Although many solvent solutions were tested (NYO-1463), none appeared promising. However, this was due in part to the fact that the alkaline materials themselves dissolved fairly readily in water.

As a result of our tests, it was suggested that hot water leaching be used to remove the bulk of the alkalinity with low uranium loss, prior to use of acid to dissolve the uranium values. Dilute acid was found to dissolve the uranium materials, leaving a solid material essentially free of uranium.

As mentioned earlier, the prime objective of the Research and Development Group was the improvement of methods for production of uranium trioxide, and this goal was reached with the completion of

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a successfully operating extraction plant using the TBP-kerosene solvent. The other projects cited were of secondary importance and work has been done only as it did not interfere with the main objective of the group and as dictated by the apparent urgency of a particular project placed on it at the time by the Atomic Energy Commission.

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