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UNITED STATES ATOMIC ENERGY COMMISSION

PROBLEMS OF REFINING URANIFEROUS
RESIDUES, ~~TECHNOLOGY~~ — ~~FEED MATERIALS~~

Progress Report No. 19 [for] November 1952

By
H. Fleck and J[ohn] E. Summers

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December 17, 1952

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AEC RESEARCH AND DEVELOPMENT REPORT

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**PROBLEMS OF REFINING URANIFEROUS RESIDUES;
TECHNOLOGY — FEED MATERIALS**

Progress Report No. 19 [for] November 1952

By H. Fleck and J. E. Summers

A. SUMMARY

GENERAL

1. Scope of Program

As of November 1, 1952, the Research Program consisted of the following projects:

Digestion and Refining of C-Slags and Other Residues (Project No. 1)

Investigate the applicability and refinement of various procedures for the treatment and digestion of C-Slags and other uraniferous residues for recovery of uranium values, placing emphasis on methods adaptable to the Canonsburg plant with minimum of change of equipment.

Refining and Processing of Sodium Carbonate Residues (Project No. 5)

Investigate methods of recovery of uranium from various residues, resulting from sodium carbonate digestion of miscellaneous uranium bearing materials, to reduce the U^{308} content of the residues below 0.05%.

2. Previous Reports

NYO-1145 March	1952 Progress Report No. 11
NYO-1146 April	1952 Progress Report No. 12
NYO-1147 May	1952 Progress Report No. 13
NYO-1148 June	1952 Progress Report No. 14
NYO-1149 July	1952 Progress Report No. 15
NYO-1150 August	1952 Progress Report No. 16
NYO-1151 September	1952 Progress Report No. 17
NYO-1152 October	1952 Progress Report No. 18

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PROJECT STATUS

3. Research Project — Digestion and Refining of C-Slags and Other Residues

Experimental work was continued on high grade feed materials. The investigation covering the feasibility of adapting C-27, Harshaw Press Cake, C-35, DC-22, Reactor Ash, and Graphite Ash to simpler processes was broadened to include sulphuric acid digestion and the recovery of solubilized uranium as sodium diuranate by neutralizing excess acid with sodium hydroxide. The purpose of all experimentation is to determine whether or not Vitro high grade feed materials can be adapted to processes of a more economical nature, as compared to the present established purification process, resulting in a satisfactory residue which would be acceptable as an end product.

A series of experiments was completed which was designed to obtain confirmation for data accumulated from previous experimentation on a prospective production process for high grade feed material. This process may be described as consisting of hydrochloric acid digestion, oxidation of the digest slurry using sodium chlorate, the removal of acid insolubles by filtration, followed by the precipitation of ammonium diuranate from the clarified filtrate by neutralization of excess acid with ammonium hydroxide and calcination of the precipitate at high temperatures to a black oxide.

Consideration was given during experimentation to the possibility of recovering dissolved uranium from a clarified hydrochloric digest filtrate by neutralizing excess acid with sodium hydroxide. If such a procedure would prove feasible it might be slightly more attractive from an economic standpoint than the use of aqua ammonia. Precipitates obtained with both ammonia and sodium hydroxide from the hydrochloric acid digest filtrate were collected by filtration and calcined at elevated temperatures approximating 800°C in order to remove halogen contamination. In this fashion a black oxide was obtained which may be satisfactory as an end product with fluorine and uranium content well within purity specifications.

In case the use of hydrochloric acid should prove to be less economical than sulphuric acid, a series of experiments was initiated which were designed to determine whether or not an acceptable product could be precipitated from a sulphuric acid digest filtrate. In effect, this procedure parallels the present Vitro purification process with the exception of the phase covering removal of sodium carbonate insoluble contaminants. Digestion of high grade feed materials was carried out in sulphuric acid solution using sodium nitrate as an oxidant. The acid insolubles were removed by filtration and excess acid was neutralized by using sodium hydroxide and the resultant precipitate was removed by filtration and calcined at 800°C. It was hoped that calcination of the precipitate at high temperatures would eliminate halogen contamination and unnecessary additional and more lengthy purification.

Additional experiments were conducted on high grade feed material using sulphuric acid digestion procedures and ammonia precipitation of uranium. Samples were digested in sulphuric acid in the presence of sodium nitrate, insolubles were removed by filtration, and ammonium diuranate precipitated by the addition of ammonium hydroxide to the acid solution. The precipitate formed was carried through the process of calcination, and the fired residue examined for contamination. The possibility of using one or both of these procedures instead of the present purification process is interesting from a standpoint of reduction of both labor and chemical cost.

Previous experimentation on DC-22 using hydrochloric acid digestive procedures had indicated that although a satisfactory product may be precipitated with ammonium hydroxide from the clarified hydrochloric acid digest filtrate, uranium content of the acid insoluble remained prohibitively high. Experiments were conducted to assay the influence of calcination of the raw material on successful extraction of contained uranium values. Other experiments were concluded in which time of digest, temperature of digest, and pH of digest were assayed as to their influence in reducing uranium content of acid insolubles to a level that would be acceptable for discard residues.

It was indicated from previous experiments on reactor ash that it would not be possible to quantitatively precipitate ammonium diuranate from a clarified acid digest filtrate due to complexing reaction of extremely high fluorine content. Experiments were conducted to determine whether or not this material could be processed by itself rather than by a process of blending with other high grade feed materials. Samples were calcined at high temperatures prior to digestion to evaluate the effect of calcination on fluoride activity. It was hoped that sufficient fluorine would be driven off so that acid filtrates would have low enough fluorine concentrations to make them amenable to ammonia precipitation. Experiments were also conducted to determine whether or not sodium hydroxide would be a successful precipitant regardless of the high fluoride content of the pregnant acid filtrate.

Previous experimentation on Harshaw Press Cake had indicated that it would be necessary to use filter aids to remove acid insolubles resulting from either a hydrochloric or sulphuric acid digest. Further experimentation was deemed necessary to determine whether or not calcination at elevated temperatures of the raw material prior to acid digestion would expedite filtration of the acid insoluble.

4. Research Project — Digestion and Refining of Sodium Carbonate Residues

Development work concerning Pitchblende Carbonate Residues was held in abeyance during the present report period in order to concentrate on experimental work on high grade feed materials.

B. DIGESTION AND REFINING OF C-OXIDE AND OTHER RESIDUES

Research Project No: 1

Research Supervisor: John E. Summers

LABORATORY OPERATIONS

5. Refining of High Grade Feed Materials by a Process of Hydrochloric Acid Digestion and Ammonia Precipitation

The search for ways and means to increase productivity under a lower unit overhead cost as regards high grade feed material was continued. Experiments had been conducted which indicated that a procedure involving hydrochloric acid digestion, oxidation with sodium chlorate, removal of acid insolubles by filtration, precipitation of uranium with aqua ammonia from a clarified filtrate, followed by calcination of the precipitate to a black oxide at high temperature might be feasible. A production process following this outline could have beneficial effect upon chemical and labor cost factors and production capacity. Preliminary data obtained from experimentation using C-27, C-35, DC-22, Graphite Ash, Harshaw Press Cake and Reactor Ash had been promising. In order to confirm these statistics, additional experiments were conducted and results may be summarized as follows:

C-27

Samples were taken from production lots and 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at approximately pH 0.5 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. Acid insolubles were removed by filtration and the clarified pregnant liquor was neutralized to pH values approximating 7.0 by using 1:1 ammonium hydroxide and "batchwise" techniques. The insoluble precipitate was removed by filtration and calcined at 800°C for one-half hour. The black oxide obtained in this manner contained less than 0.1% fluoride and more than 95% U³⁰⁸. Uranium content of acid insolubles averaged less than 0.05% U³⁰⁸.

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Harshaw Press Cake

Samples were taken from production lots and 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at pH 0.0 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. Filtration of acid insolubles resulting from the hydrochloric digest of this material continues to be a problem unless commercial filter aids are present. Filtration of the insoluble without the filter aids is almost impossible. Uranium was precipitated from the clarified filtrate by neutralization of excess acid with aqua ammonia at pH 7.0. The precipitate was collected by filtration and calcined to a black oxide at 800°C. As indicated by previous results, the resultant product is well within purity specifications containing less than 0.1% F and more than 90% U³⁰⁸. Acid insolubles in most instances were in excess of purity specifications for discard. Presumably, solubilized uranium was retained in the acid insoluble residue by occlusion due to the slimy nature of the residue. To obtain discard residues containing less than 0.05% U³⁰⁸ it is possible that on a production level a repulp wash of acid insolubles will be necessary.

C-35

Additional experiments performed on this material confirm previous experimental data. Samples were taken from production lots and 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at approximately pH 0.5 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. Acid insolubles were removed by filtration and uranium was precipitated at pH 7.0 by using ammonium hydroxide. Ammonium diuranate was collected by filtration and was calcined at 800°C. The black oxide obtained in this manner contained less than 0.1% F and more than 90% U³⁰⁸.

DC-22

Preliminary data had indicated that in so far as the end product is concerned DC-22 was amenable to a process consisting of hydrochloric acid digestion, oxidation by sodium chlorate, removal of acid insolubles by filtration and precipitation of the contained uranium from the clarified acid filtrate with ammonium hydroxide. However, acid insoluble discard residues contained uranium values considerably in excess of purity specifications. To confirm this, samples were taken from production lots and 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at approximately pH 0.0 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. After removal of acid insolubles by filtration, uranium was precipitated from the filtrate in the usual manner using ammonium hydroxide. Calcination of the resultant precipitates to a black oxide, and subsequent analysis, indicated a product of high purity with uranium content exceeding 90% U³⁰⁸ and halogen

content remaining less than 0.1% F. However, uranium continued to be present in the acid insoluble in excessive amounts up to 0.5% U^{308} , which is well beyond specifications for discard residues. Experiments designed to reduce uranium content of the hydrochloric acid insoluble residue to within purity specifications were conducted and are reported under paragraph 9 in this report. Despite inadequate extraction, confirmation of the quality of the end product was obtained.

Reactor Ash

Data obtained from concluded experiments had indicated that a process of hydrochloric acid digestion, oxidation by sodium chlorate for three hours at 90°C would be a satisfactory procedure for extracting uranium values and reducing uranium content of the acid insoluble residues to less than 0.05% U^{308} . However, it would not be possible to use ammonium hydroxide for quantitative precipitation of solubilized uranium due to the complexing action of the exceedingly high fluorine content of the pregnant liquor. In order to varify these results samples were taken from production lots and 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at approximately pH 0.5 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. When ammonia was added to the clarified filtrate in excess amounts up to pH 8.0–8.5 quantitative precipitation of contained values was not obtained. Since apparently this procedure will not be feasible as regards reactor ash, experiments concerning other precipitants and process techniques were conducted in order to obtain maximum extraction, and are reported under paragraph 10.

Graphite Ash

Preliminary results of experiments conducted on this material indicated that a process of hydrochloric acid digestion, oxidation by sodium chlorate, followed by removal of acid insolubles by filtration and precipitation of solubilized uranium using ammonium hydroxide would be satisfactory in obtaining an end product of high purity. Additional experiments using identical procedures generally confirm accumulated results. 500 gram samples of production lots were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid at approximately pH 0.0 in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. Acid insolubles were removed by filtration and the pregnant clarified acid solution was neutralized with ammonium hydroxide to pH values approximating 7.0. The resultant precipitate was collected by filtration and when calcined to a black oxide at temperatures approximating 800°C was found to be an end product of high purity containing more than 95% U^{308} and less than 0.1% F. However, filtration of the acid insoluble residue is somewhat slow without the use of filtering aids. Due to the slimy nature of the residue the acid insolubles contained uranium values slightly exceeding 0.05% U^{308} . Presumably, either filtering aids or a repulp wash of acid insolubles will be necessary to obtain discard residues containing less than 0.05% U^{308} .

An overage of all experimental data obtained during the present report period, from experimentation on high grade feed material using the hydrochloric acid digestive procedure followed by precipitation of ammonium diuranate, is tabulated and presented in Table I.

6. Refining of High Grade Feed Material Using a Process of Hydrochloric Acid Digestion Followed by Precipitation of Uranium Using Sodium Hydroxide

Consideration was given to sodium hydroxide as precipitant of uranium from the pregnant hydrochloric acid digest filtrates obtained under digestive procedures already outlined. The process consists of digestion in 15° Baume commercial hydrochloric acid in the presence of 0.5% (w/v) sodium chlorate as an oxidizing agent and the removal of the acid insolubles by filtration prior to precipitation of contained uranium values. It was believed the use of sodium hydroxide rather than aqua ammonia might prove slightly more attractive from an economic standpoint. Precipitate residues obtained using caustic soda as a precipitant were considered as a product before and after calcination at 800°C. Generalized results indicate that a satisfactory product cannot be obtained without calcination. Although uranium content of uncalcined residues is satisfactory, fluoride content remains prohibitively high. From a production standpoint another attractive feature of caustic precipitation would be a product which is more readily filtered than ammonium diuranate. Experiments were conducted on the samples of production lots used for experimentation on the precipitation of ammonium diuranate. Preliminary results may be summarized as follows:

C-27

500 gram samples of pulverized material were slurried in 2000 ml of water and carried through a digestive procedure consisting of digestion in 15° Baume commercial hydrochloric acid and oxidation using 0.5% (w/v) sodium chlorate followed by removal of acid insolubles by filtration. The pregnant clarified liquor resulting from this procedure was neutralized to pH values approximating 7.0 using a 1:1 solution of sodium hydroxide. The precipitate formed was removed by filtration, washed and analyzed prior to and after calcination at 800°C. Preliminary results indicate that without calcination fluoride content of the resultant product will remain far in excess of purity specifications containing fluorides in proportions up to 2½%. Consideration of the product obtained in this manner after calcination at 800°C indicates that while this procedure is not as effective in eliminating halogen contamination as precipitation with aqua ammonia, never the less the product is within specifications containing less than 0.5% F.

Harshaw Press Cake

500 gram samples from production lots were slurried in 2000 ml of water, digested in 15° Baume commercial hydrochloric acid and oxidized using 0.5% (w/v) sodium chlorate for three hours at 90°C. The clarified filtrates obtained by removal of the acid insolubles by filtration, expedited by the use of commercial filter aids, were neutralized to pH values approximating 7.0–7.2 using 1 : 1 solution of sodium hydroxide. The resultant precipitate was removed by filtration and analyzed before and after calcination at 800°C. While the product contained satisfactory quantities of uranium it contained excessive amounts of fluorine, but after calcination to a black oxide at 800°C the fluorine content was reduced below maximum level and averaged less than 0.5% F.

C-35

Samples of C-35 from production lots were treated in a similar manner. 500 gram portions were slurried in 2000 ml of water and digested in 15° Baume commercial hydrochloric acid in the presence of 0.5% (w/v) sodium chlorate for three hours at 90°C. Clarification of the filtrate was effected through filtration. A residue satisfying purity specifications for an acceptable end product was obtained by neutralizing excess acid with sodium hydroxide, removing the resultant precipitate by filtration, and calcining the residue at 800°C. Uranium content was considerably in excess of minimum requirements, averaging over 85% U^{308} , and fluoride contamination did not exceed 0.5% F.

DC-22

500 gram portions of DC-22 from production lots were slurried in 2000 ml of water, digested in 15° Baume hydrochloric acid at pH values approximating 0.0 in the presence of 0.5% (w/v) sodium chlorate at 90°C for three hours. After removal of acid insolubles by filtration, the clarified filtrate was neutralized to pH 7.0 using a 1:1 sodium hydroxide solution. The precipitate that was formed was collected by filtration, washed, and portions were calcined at elevated temperatures approximating 800°C. An analysis of the resultant residue indicated a satisfactory end product with uranium values in excess of 90%, and fluoride contamination within maximum specifications of 0.5%. However, prior to calcination, the residue contained excessive quantities of fluorine and must be considered an unsatisfactory end product.

Reactor Ash

Samples from production lots of Reactor Ash were treated in a similar manner. It was hoped that by using sodium hydroxide as a precipitant that it would be possible to obtain quantitative precipitation from the clarified acid filtrate resulting from hydrochloric acid digestion regardless of the complexing

action of the large quantities of fluorine in the pregnant liquor. Digestion was carried out in a normal manner by slurrying 500 gram samples in 2000 ml of water, digesting in 15° Baume hydrochloric acid in the presence of 0.5% (w/v) sodium chlorate at low pH values for periods of time up to three hours at 90°C. Acid insolubles were removed by filtration and found to contain less than 0.05% U^{308} . The clarified pregnant liquor was neutralized using a 1:1 sodium hydroxide solution at pH values ranging from 7.0–7.5. The precipitates resulting from this treatment were collected by filtration, washed and calcined at 800°C. Consideration of the discard effluent resulting from precipitation indicated that this is a more effective means of precipitating uranium from a high fluoride solution than using ammonia. However, the effluent contained excessive amounts of uranium. Present specifications for discard effluents were exceeded. The product obtained by calcination at high temperature was a satisfactory product in so far as uranium and fluoride content are concerned. Uranium values exceeded 75% U^{308} and fluoride content was less than 0.5%. The product prior to calcination contained excessive quantities of halogens.

Graphite Ash

500 gram portions of Graphite Ash were treated in a similar manner. The samples were slurried in 2000 ml of water, digested in 15° Baume hydrochloric acid in the presence of 0.5% (w/v) sodium chlorate at pH values approximating 0.0 for three hours at 90°C. Filtration of acid insolubles was somewhat slow but was expedited through the use of commercial filter aids. The pregnant liquor was neutralized using 1:1 sodium hydroxide solution, and the product thus obtained, after collection by filtration and calcination at 800°C, contained more than 80% U^{308} and less than 0.5% fluorine. Again, prior to calcination, contamination due to halogens was excessive.

Data obtained from the processing of high grade feed materials by hydrochloric acid digestion and precipitation of solubilized uranium using sodium hydroxide was tabulated, averaged, and may be found in Table II.

7. Refining of High Grade Feed Materials Using a Process of Sulphuric Acid Digestion and Precipitation of Solubilized Uranium with Ammonium Hydroxide

One of the factors in assuming that hydrochloric acid digestive procedures for high grade feed materials would be attractive was the possibility of obtaining low cost AEC acid. Should this assumption not prove to be valid, it still may be possible to improve or simplify the established Vitro purification process, in so far as economic factors are concerned, by eliminating the carbonation phase designed to remove contaminants of the R_2O_3 group. The possibility of a process composed of sulphuric acid digestion, removal of acid insolubles by filtration, and the precipitation of solubilized values by neutralizing excess acid with ammonium hydroxide has been considered. Preliminary steps have been taken to

determine whether or not a process of this nature would result in an end product which would satisfy all purity specifications with regard to uranium content and halogen contamination. Samples of production lots were used for experimentation. High grade feed materials under consideration consist of C-27, C-35, DC-22, Harshaw Press Cake, Graphite Ash, and Reactor Ash. Preliminary experiments have been completed and the cumulated results to date are:

C-27

500 gram samples of C-27 were taken from production lots, pulverized to 100 mesh, slurried in 2000 ml of water and digested in sulphuric acid at pH values approximating 0.0 to 0.5, oxidized by the addition of sodium nitrate and filtered to remove acid insolubles. The clarified filtrate was neutralized to pH values from 6.5-7.0 using 2:1 ammonium hydroxide and "batch" techniques of precipitation. The residue obtained in this fashion was collected by filtration, washed and calcined to a black oxide at 800°C. Preliminary results indicate that a treatment of this nature may be feasible in obtaining a satisfactory end product. Preliminary data indicates a uranium level in excess of 95% U^{308} and fluoride content well below maximum specification of 0.5%. Analysis of ammonium diuranate prior to calcination indicated that it would not be a satisfactory product due to excessive halogen contamination.

C-35

In the same manner, 500 gram samples of C-35 were collected from production lots, slurried in 2000 ml of water, digested in sulphuric acid at low pH values, oxidized by using 1% (w/v) sodium nitrate, neutralized by using ammonium hydroxide at pH 7.0 after removing acid insolubles by filtration. Uranium level of the insoluble residue was below maximum specification for discard residues. The precipitate formed by the addition of ammonia was collected by filtration and calcined to a black oxide at 800°C. Analysis before and after calcination indicates that the fired product will be satisfactory in so far as halogen contamination and uranium content are concerned, but as indicated by previous experimentation the ammonium diuranate contains excessive quantities of fluorine.

Harshaw Press Cake

500 gram samples of Press Cake were obtained and slurried in 2000 ml of water and digested in sulphuric acid in the presence of sodium nitrate at low pH values for three hours at 90°C. As expected, when using this digest media, filtration of the acid insolubles without use of filtering aids continues to be extremely difficult, if not impossible. Clarified filtrates for precipitation were obtained by the use of filter aids and the centrifuge. Uranium content of the insoluble residue exceeded maximum specifications for discard residues and

this must be attributed to the filtering characteristics of the insolubles. Ammonium diuranate, when precipitated from the clarified acid filtrate by the addition of 2 : 1 ammonium hydroxide at pH values approximating 7.0 and calcined at 800°C formed a black oxide of high uranium content and low fluorine contamination suitable for an end product. The ammonium diuranate prior to calcination, while containing uranium values exceeding minimum specifications, as expected, contained a large proportion of fluorides.

DC-22

500 gram samples of pulverized material were slurried in 2000 ml of water, digested in sulphuric acid at pH 0.0 in the presence of 1% (w/v) sodium nitrate for three hours at 90°C. After removal of the acid insolubles by filtration, the clarified filtrate was used for experimentation. Uranium and other insoluble hydroxides were precipitated from the pregnant liquor at approximately pH 7.0 by using 1 : 1 ammonium hydroxide. The product obtained from this procedure when calcined at 800°C was acceptable in every manner as an end product. Uranium content exceeded 80% U^{308} and fluorine level was less than 0.2%. In this instance, as in hydrochloric acid digestion, uranium content of the acid insoluble remained excessively high. Experiments designed to lower uranium content of acid insolubles to a discard level have been initiated and are reported under paragraph 9.

Graphite Ash

500 gram samples of graphite ash were submitted to identical treatment. The process consisted of slurrying 500 gram samples of pulverized material in 2000 ml of water, digesting in sulphuric acid at pH 0.0, oxidizing with 1% (w/v) sodium nitrate, removing acid insolubles by filtration and precipitating uranium from the clarified filtrate by the addition of 1 : 1 ammonium hydroxide. The precipitate, when collected, washed and calcined at 800°C, exhibited superior characteristics as regards uranium and fluoride content. Filtration of the acid insolubles was somewhat slow unless expedited with commercial filter aids. Uranium content of acid insolubles exceeded maximum specifications for discard residues due to slime forming characteristics and they would probably have to be repulp washed to reduce uranium content to a discard level.

Reactor Ash

Sulphuric acid digestion and purification of reactor ash was undertaken in the same manner. 500 gram samples were slurried in 2000 ml of water, digested in sulphuric acid, oxidized with 1% (w/v) sodium nitrate, and the slurry clarified by filtration. Acid insolubles contained less than 0.05% U^{308} . Ammonium diuranate was precipitated from the clarified liquor by the addition of ammonium hydroxide to pH 7.5. As in the case of hydrochloric acid digestion

and ammonia precipitation, removal of uranium was not quantitative due to the presence of large amounts of fluorine and its complexing action. However, the insoluble hydroxides removed in this manner when calcined at 800°C were satisfactory as an end product as regards both uranium and fluoride specifications.

All data concerning sulphuric acid digestion of high grade feed material and subsequent precipitation of uranium from a clarified filtrate using ammonia was averaged, tabulated and is presented in Table III.

8. Refining of High Grade Feed Materials by a Process of Sulphuric Acid Digestion and Precipitation of Uranium Using Sodium Hydroxide

As in the case of hydrochloric acid digestive procedures, it was deemed advisable to test the efficiency of sodium hydroxide as a precipitant for possible application to the simpler procedure. If successful, it would probably be a more satisfactory reagent from a standpoint of economics and filterability of the resultant precipitate. The sulphuric acid digestive procedure that was used was identical to that reported above. Samples were digested in commercial sulphuric acid at pH values ranging from 0.0–0.5, sodium nitrate was used as an oxidizing agent, acid insolubles were removed by filtration and the clarified filtrate resulting from this procedure was used for experimentation. Commercial sodium hydroxide was used as a precipitant after solubilizing in water at a ratio of 1:1. Preliminary statistics as indicated to date are as follows:

C-27

500 gram samples of C-27 were slurried in 2000 ml of water, digested in sulphuric acid at pH 0.5 in the presence of 1% (w/v) sodium nitrate for three hours at 90°C. Acid insolubles were removed by filtration and found to contain less than 0.05% U^{308} , a satisfactory level for discard residues. The clarified filtrate resulting from this procedure were neutralized to approximately pH 7.0 using sodium hydroxide and the precipitate that was formed was collected by filtration and calcined at 800°C. In this instance, as in every other instance, both uranium and fluoride concentrations met purity specifications for an end product.

C-35

Samples of C-35 were carried through the outlined digestive procedure consisting of sulphuric acid treatment, sodium nitrate oxidation, and removal of acid insolubles by filtration. Acid insolubles resulting from the sulphuric acid digest were somewhat bulky but were easily removed by filtration and contained less than 0.05% U^{308} . Sodium hydroxide was used to precipitate solubilized uranium values from the pregnant liquor and the resultant precipitate was calcined at 800°C after collection by filtration. The black oxide resulting from the calcination treatment was in every way a satisfactory product, containing more than 90% U^{308} and less than 0.5% F.

Harshaw Press Cake

As previously indicated, acid digestion of 500 gram samples of Press Cake resulted in an insoluble residue that was not filterable until expedited with commercial filter aids. As in every other instance, uranium content of the insoluble level remained above maximum specifications for discard residues and would probably have to be further reduced by repulp washing. The product obtained from the pregnant liquor by neutralizing excess acid with commercial sodium hydroxide was calcined at elevated temperatures to form a black oxide conforming to purity specifications as regards both uranium and halogen content.

DC-22

When 500 gram samples of DC-22 were slurried in 2000 ml of water and digested in sulphuric acid at low pH values in the presence of sodium nitrate uranium content of the insoluble residue exceeded specifications. An exceptionally bulky insoluble residue was formed but was easily removed by filtration. When the pregnant liquor resulting from the acid treatment was used for experimentation, the insoluble precipitate formed by the addition of sodium hydroxide was a satisfactory end product when calcined at 800°C. Uranium content was well above minimum specifications and fluoride content of the compound was well below 0.5% fluorine.

Reactor Ash

500 gram samples of reactor ash were processed by a sulphuric acid procedure identical to the procedure outlined above. After slurring pulverized samples in 2000 ml of water, digestion was carried out in a sulphuric acid sodium nitrate media. After digestion for three hours at 90°C the insolubles were removed by filtration. Uranium content of the acid insolubles was within specifications containing less than 0.05% U^{308} . When the clarified filtrate obtained in this manner was neutralized by using sodium hydroxide to pH 7.5 quantitative precipitation of solubilized uranium was not obtained. The product as precipitated was calcined at elevated temperature, analyzed, and found to contain uranium values exceeding minimum specification and less halogen contamination than specified as maximum.

Graphite Ash

When graphite ash samples were processed in identical manner using sulphuric acid digestive procedures followed by the precipitation of uranium from the pregnant liquor by sodium hydroxide, a residue was obtained which when calcined at 800°C met purity specifications in all respects. As previously indicated, filtration of acid insolubles was abnormally slow unless expedited through the use of filter aids. Also, repulp washing of the insoluble residue was necessary to reduce uranium content of the insoluble residue to less than maximum specifications for discard residues.

Preliminary data concerning the purification of high grade feed materials using a process of sulphuric acid digestion, followed by precipitation of uranium from a clarified filtrate by the addition of sodium hydroxide have been averaged, tabulated, and may be found in Table IV.

9. Experiments Concerning Optimum Digestive Factors for the Extraction of Uranium from DC-22 Using Mineral Acids

Previous experimental data had indicated that it would be necessary to conduct an investigation to determine what factor or factors involve successful and optimum extraction of uranium from DC-22 using mineral acids. A series of experiments was completed in which various factors such as temperature of calcination of raw material, pH of digestion, and digest time were reviewed to determine what techniques would be effective in reducing uranium content of insoluble residues resulting from hydrochloric acid digestion below the maximum uranium content specifications for a discard residue. 100 gram samples taken from production lots of DC-22 were calcined at varied temperature, slurried in water at a ratio of 4:1, and digested in hydrochloric acid at varied pH values over variable periods of time. Experimental data indicates that calcination temperatures approximating 1400°F will be effectual in providing optimum extraction of uranium from the raw material using hydrochloric acid. Neither protracted periods of digest time nor excess quantities of acid will be necessary to obtain satisfactory extraction if the raw material is calcined at the indicated temperature for one hour prior to digestion. Representative data may be found in Table V.

10. Experiments Designed to Determine Whether or Not Quantitative Precipitation of Uranium May Be Obtained from a Pregnant Liquor Resulting from Hydrochloric Acid Digestion of Reactor Ash

Preliminary experiments have been initiated to determine what techniques will be necessary to prepare the raw material for an acid digestion which will result in a clarified filtrate not containing excessive quantities of fluorine which would prevent quantitative precipitation of solubilized uranium. 100 gram samples of reactor ash were calcined at temperatures exceeding 800°C in order to determine whether or not sufficient fluorine could be driven off prior to digestion so that quantitative recovery of solubilized uranium from the pregnant liquor would be possible. To date, although calcining the raw material prior to digestion has been successful to the extent that recovery of solubilized values has improved, discard effluents still remained excessively high, up to 0.1% U^{308} , and exceeded the present Vitro specifications for a discard effluent.

Additional experiments were completed in which the influence of pH of precipitation was assayed. Sodium hydroxide was added as a precipitant to a clarified acid filtrate in excess amounts to pH 12.0. It was found that at pH 10.5,

quantitative recovery could be obtained with discard effluent averaging 0.002% U^{308} . The precipitate obtained by this procedure was collected by filtration, and calcined at 800°C. Uranium content of the product of this procedure was in excess of 75% U^{308} and contained less than 0.5% F. Preliminary data may be found in Table VI.

C. REFINING AND PROCESSING OF SODIUM CARBONATE RESIDUES

Research Project No: 5

Research Supervisor: John E. Summers

LABORATORY OPERATIONS

11. Development of Processes for the Extraction of Uranium from Sodium Carbonate Residues Resulting as a By-Product of Pitchblende Purification

Developmental work on Pitchblende Carbonate Residues has been held in abeyance during this period in order to concentrate on prospective processes for the purification of high grade feed material. An extensive experimental program surveying the applicability of various processes for these residues is planned for the next report period.

Table I—Extraction of Uranium by Hydrochloric Acid Digestion Followed by the Precipitation of Ammonium Diuranate

Material: High Grade Feed Material

Mesh: 85% -100

	Material					
	C-27	DC-22	C-35	Reactor Ash	Press Cake	Graphite Ash
Weight of sample (gm)	500	500	500	500	500	500
Weight of H ₂ O (gm)	2000	2000	2000	2000	2000	2000
Weight of HCl (gm)	550	865	565	425	410	462
Digest pH	0.5	0.0	0.5	0.5	0.0	0.0
NaClO ₃ used to oxidize (gm)	1.5	2.0	1.75	1.25	1.25	1.50
Digest time (hr)	3	3	3	3	3	3
Digest temperature (°C)	90	90	90	90	90	90
Acid insolubles (gm)	105	125	90	237	210	95
Acid insolubles (% U ³⁰⁸)	0.050	0.44	0.035	0.050	0.21	0.075
Precipitant	NH ₄ OH	NH ₄ OH	NH ₄ OH	NH ₄ OH	NH ₄ OH	NH ₄ OH
pH of precipitation	7.0	7.0	7.0	8.25	7.0	7.0
Discard effluent (% U ³⁰⁸)	0.0005	0.0007	0.0002	0.38	0.0001	0.0007
Ammonia salts (% U ³⁰⁸)	86.2	81.68	83.21	52.86	85.24	82.86
Ammonia salts (% F)	2.55	1.65	1.80	4.21	1.13	0.11
Calcination temperature for ammonia salts (°C)	800	800	800	800	800	800
Black oxide (% F)	0.062	0.026	0.016	0.32	0.020	0.002

Table II—Extraction of Uranium by Hydrochloric Acid Digestion
Followed by the Precipitation of Sodium Diuranate

Material: High Grade Feed Material

Mesh: 85% -100

	Material					
	C-27	DC-22	C-35	Reactor Ash	Press Cake	Graphite Ash
Weight of sample (gm)	500	500	500	500	500	500
Weight of H ₂ O (gm)	2000	2000	2000	2000	2000	2000
Weight of HCl (gm)	550	865	565	425	410	452
Digest pH	0.5	0.0	0.5	0.5	0.0	0.0
Sodium chlorate to oxidize (gm)	1.5	2.0	1.75	1.25	1.25	1.50
Digest time (hr)	3	3	3	3	3	3
Digest temperature (°C)	90	90	90	90	90	90
Acid insolubles (gm)	105	125	90	237	210	95
Acid insolubles (% U ³⁰⁸)	0.05	0.44	0.035	0.050	0.21	0.075
Concentration NH ₄ OH: H ₂ O	1:1	1:1	1:1	1:1	1:1	1:1
pH of precipitation	7.0	7.0	7.0	7.0	7.0	7.0
Discard effluent (% U ³⁰⁸)	0.0002	0.0003	0.0007	0.26	0.0005	0.0005
NaOH precipitate (% U ³⁰⁸)	86.6	78.82	76.72	61.52	76.49	82.65
NaOH precipitate (% F)	1.31	1.60	0.96	2.53	1.32	0.29
Calcination temperature for precipitate (°C)	800	800	800	800	800	800
Black oxide (% U ³⁰⁸)	95.62	89.62	86.4	75.42	82.66	93.42
Black oxide (% F)	0.38	0.37	0.34	0.42	0.32	0.03

Table III—Extraction of Uranium By Sulphuric Acid Digestion
Followed by the Precipitation of Ammonium Diurante

Material: High Grade Feed Material

Mesh: 85% -100

	Material					
	C-27	DC-22	C-35	Reactor Ash	Press Cake	Graphite Ash
Weight of sample (gm)	500	500	500	500	500	500
Weight of H ₂ O (gm)	2000	2000	2000	2000	2000	2000
Weight of H ₂ SO ₄ (gm)	380	1025	760	665	600	400
Digest pH	0.0	0.0	0.0	0.0	0.0	0.0
Sodium nitrate to oxidize (gm)	2.75	3.5	3.0	3.0	3.0	3.0
Digest time (hr)	3	3	3	3	3	3
Digest temperature (°C)	90	90	90	90	90	90
Acid insolubles (gm)	140	260	60	275	250	106
Acid insolubles (% U ³⁰⁸)	0.046	0.32	0.026	0.050	0.16	0.11
Concentration of NH ₄ OH : H ₂ O	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
pH of precipitation	7.0	7.0	7.0	7.5	7.0	7.0
Discard effluent (% U ³⁰⁸)	0.0003	0.0001	0.0001	0.35	0.0005	0.0001
NH ₄ OH precipitate (% U ³⁰⁸)	83.72	77.84	80.08	59.86	75.37	82.32
NH ₄ OH precipitate (% F)	0.56	2.28	1.31	1.40	0.42	0.42
Calcination temperature for precipitate (°C)	800	800	800	800	800	800
Black oxide (% U ³⁰⁸)	90.68	90.18	89.60	69.44	87.92	95.26
Black oxide (% F)	0.009	0.15	0.018	0.42	0.020	0.14

Table IV — Extraction of Uranium by Sulphuric Acid Digestion
Followed by the Precipitation of Sodium Diuranate

Material: High Grade Feed Material
Mesh: 85% -100

	Material					
	C-27	DC-22	C-35	Reactor Ash	Press Cake	Graphite Ash
Weight of sample (gm)	500	500	500	500	500	500
Weight of H ₂ O (gm)	2000	2000	2000	2000	2000	2000
Weight of H ₂ SO ₄ (gm)	380	1025	760	665	600	400
Digest pH	0.0	0.0	0.0	0.0	0.0	0.0
Sodium nitrate to oxidize (gm)	2.75	3.5	3.0	3.0	3.0	3.0
Digest time (hr)	3	3	3	3	3	3
Digest temperature (°C)	90	90	90	90	90	90
Acid insolubles (gm)	140	260	60	275	250	106
Acid insolubles (% U ³⁰⁸)	0.046	0.32	0.026	0.050	0.16	0.11
Concentration of NH ₄ OH: H ₂ O	1:1	1:1	1:1	1:1	1:1	1:1
pH of precipitation	7.0	7.0	7.0	7.5	7.0	7.0
Discard effluent (% U ³⁰⁸)	0.0003	0.0003	0.0005	0.24	0.0007	0.0006
NaOH precipitate (% U ³⁰⁸)	76.21	74.48	72.68	56.8	75.60	82.00
NaOH precipitate (% F)	1.51	0.61	0.63	2.98	0.69	0.42
Calcination temper- ature for precipitate (°C)	800	800	800	800	800	800
Black oxide (% U ³⁰⁸)	89.04	93.52	84.21	67.50	82.60	90.20
Black oxide (% F)	0.13	0.034	0.008	0.23	0.009	0.019

Table V—Experiments Concerning Acid Digestion of DC-22

Mesh: 85% U_3O_8

	Experiment Number							
	1	2	3	4	5	6	7	8
Weight of sample	100	100	100	100	100	100	100	100
Weight of H_2O	400	400	400	400	400	400	400	400
Weight of HCl	170	170	170	170	170	170	170	170
Calcination temperature of raw material ($^{\circ}C$)	1000	1000	1000	1200	1200	1200	1400	1400
pH of digestion	0.0	0.0	0.5	0.0	0.0	0.5	0.0	0.0
Temperature of digestion ($^{\circ}C$)	90	90	90	90	90	90	90	90
Time of digestion (hr)	3	6	3	3	6	3	3	6
Acid insolubles (% U^{308})	0.66	0.42	0.84	0.24	0.11	0.36	0.05	0.032

Table VI—Extraction of Uranium from Reactor Ash

Mesh: 85% -100

	Experiment Number				
	1	2	3	4	5
Weight of sample (gm)	100	100	100	100	100
Weight of H ₂ O (gm)	400	400	400	400	400
Weight of HCl (gm)	85	85	85	85	85
Calcination temperature of raw material (°C)	800	800			
Precipitant	NaOH	NaOH	NaOH	NaOH	NaOH
pH of precipitation	7.0	7.5	8.5	10.5	12.0
Discard effluent (% U ³⁰⁸)	0.16	0.119	0.01	0.0026	0.0007
Calcination temperature of precipitate (°C)	800	800	800	800	800
Black oxide (% U ³⁰⁸)	56.8	55.46	69.41	75.21	74.89
Black oxide (% F)	0.34	0.22	0.42	0.23	0.26