STUDIES REGARDING THE ROLE OF WYOMING NATURAL GAS IN PRECIPITATING PRIMARY URANIUM MINERALS FROM PREGNANT SOLUTIONS

Project No. 550837

By
Harry M. Sims
Fred L. Smith

May 11, 1956

Colorado School of Mines Research Foundation, Inc.
Golden, Colorado

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STUDIES REGARDING THE ROLE OF WYOMING NATURAL GAS IN PRECIPITATING PRIMARY URANIUM MINERALS FROM PREGNANT SOLUTIONS

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Golden, Colorado

Project No. 550837
May 11, 1956

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ABSTRACT AND CONCLUSIONS

There is reason to believe that natural gases may play a role in the formation of uranium deposits such as occur in the Gas Hills Area of Wyoming. This project was designed to test the chemical feasibility of depositing a primary uranium mineral from a pregnant solution by exposing the solution to natural gas in an environment favorable to such deposition. The first phase of this project was concerned with a study of reactions under simulated, but accelerated, conditions.

It is feasible that natural gas found in nature may effect the reduction, and subsequent precipitation, of uraninite from pregnant aqueous solutions. It is felt that this action is due mainly to the high reducing power of the hydrogen sulfide present in the gas. This opinion is based on the experimental evidence that "desulfurized" natural gas, i.e., natural gas with hydrogen sulfide removed, did not give the high yields shown by hydrogen sulfide gas.

Further, it is felt that the mechanism in the precipitation of uraninite from aqueous solutions is mainly the reduction of uranium-plus six ion to uranium-plus four; therefore, the reducing power of the reagents in contact is a controlling factor. This is substantiated by the very high yield when using iron filings which generate considerable hydrogen gas (H₂). The hydrogen gas is a good reducing agent; the percentage yield was 70.29 per cent. Indications are that if a considerable excess of hydrogen were maintained the yield would approach 100 per cent. Further proof lies in the comparative yield of
solutions in contact with $\text{H}_2\text{S}$ which was between 36 per cent and 44 per cent, or roughly one-half the yield with hydrogen gas. Experiments in which the ratio of uranium to ferrous iron was varied over a tenfold range show that while the ferrous ion has some reducing effect, it is not in itself sufficient to drive the reaction to completion.

To sum up we offer the following tentative conclusions:

1. Primary uranium minerals can be precipitated from pregnant solutions by natural gas.

2. This precipitation is achieved by reduction of soluble hexavalent uranium salts to insoluble tetravalent compounds. The reducing agent is primarily the hydrogen sulfide present in the natural gas, but hydrogen, and perhaps methane, in the gas, and ferrous ions in the pregnant solutions contribute to the reaction.

These are the more important conditions which seem to control the deposition, through reduction, of uraninite from aqueous solutions of uranyl salts. These conditions fit those set up in the field, either directly or indirectly, by the presence of natural gas with high hydrogen sulfide content.
BACKGROUND OF THE WORK

Credit for conceiving the idea that natural gases are important in the deposition of uranium belongs to Mr. Eugene W. Grutt, Jr. of the Casper Sub-Office, U. S. Atomic Energy Commission, Division of Raw Materials, Casper, Wyoming.

The project was initiated on August 1, 1955, by contract between the Colorado School of Mines Research Foundation and the Atomic Energy Commission. Discussions between personnel of these two organizations were held in order to develop a specific plan of attack and to exchange information. It was decided to work only with ores from the Gas Hills Area.

A brief survey of available literature revealed no work of a similar nature. The work by John Gruner at the University of Minnesota on the synthesis of uranium minerals was helpful but had not been undertaken to investigate the specific effect of natural gas.

The initial efforts were to simulate experiments, as outlined by Gruner's report, (1) which would utilize elevated temperatures and a hydrogen sulfide atmosphere to reduce chemically aqueous solutions of uranyl sulfate and ferrous sulfate. This procedure should result in the formation of a uraninite precipitate.

A geologic reconnaissance survey was made by Mr. R. B. Travis on August 26-28, 1955, in order to observe the ore deposits and their relations to the gas seeps and host rocks and to collect samples of the various materials for the testwork to be conducted by the Research Foundation.

Description of Areas Examined

Gas Hills Area

The Gas Hills Area is located in Fremont and Natrona Counties in central Wyoming in the Wind River Basin. A general description of the area is given in U.S.G.S. Circular No. 352 by J. D. Love.

Lucky Mac Mine

The Lucky Mac Mine was the initial discovery area. It is located on the southwest flank of the Gas Hills anticline. Ore occurs in highly feldspathic sands of the Wind River formation. These sands are argillaceous and conglomeratic, passing abruptly into conglomerates in many places. Grey calcareous zones and highly oxidized yellow and brown zones are erratically distributed. The formation is highly lenticular, and lenses of clay or mudstone are common. It is impossible to recognize ore even with a counter. Consequently, the ore body has not yet been outlined, even though a large area was drilled on 50-foot spacings. Selenium, molybdenum, and arsenic are also present.
Cochan Mine

This mine is located in Section 3, T 32N, R 94W, Fremont County, Wyoming, on the Beaver Plateau on the west flank of the Conant Creek anticline. The ore occurs in the upper and middle Eocene sediments which are lithologically similar to the Wind River formation except for volcanic material. The ore contains much bituminous, asphaltic, and tar material. The ore is underlain by hard blue calcareous mudstone and grit. Some unidentified constituent of the ore fluoresces a red color.

Gas Hills Gas Seep

At the north end of the Gas Hills anticline, gas and a little water seep to the surface in alluvium over an area about 50 feet in diameter. At the time the site was visited, about three puddles were bubbling steadily. These puddles of water were about 1 foot in diameter and were located in soft marshy areas 10 to 20 feet in diameter. Many smaller puddles would occasionally give off some gas. A crust of caliche-like material covers some of the marshy areas, but below the crust there is very soft, black bituminous mud or grey bituminous-free mud. A thin coating of soft black material is currently being precipitated. This material, the water, and the gas give off an odor similar to that of hydrogen sulfide, but the black mud has a distinct petroleum odor. Lead acetate test paper was blackened in the gas showing that hydrogen sulfide was present.
Vitro Mine

This mine is one of the most active. It is located toward the southern end and near the axis of the Gas Hills anticline. The stratigraphy and ore are the same as that of the Lucky Mac, and it is believed that the mines will prove to be on the same ore body. The present ore, which is said to run as high as 10 per cent U₃O₈, is at the bottom of the large drop cut.

Sample Description

The following is a list of samples of rock, gas, and water collected in the Gas Hills uranium area and Fremont and Natrona Counties, Wyoming, by R. B. Travis on August 26 and 27, 1955.

**GHLM-1 - Lucky Mac Mine.** Wind River formation. Yellow to grey, friable, argillaceous conglomeratic, feldspathic coarse sand or grit. Found about 18 inches above a 1/2-inch carbonaceous layer and 20 feet above black bituminous material of GHLM-3. Count on sand was 0.2 milliroentgen per hour (mr/hr) but the sand is not ore.

**GHLM-2 - Lucky Mac Mine.** Same lithology as GHLM-1; somewhat more limonite stained. Carbonaceous material and remnantal boulders of GHLM-8-type rock common. The sample was taken about 10 feet above black bituminous layer of GHLM-3. The face from which sample was taken counts 0.5 mr/hr, but is not ore.

**GHLM-3 - Lucky Mac Mine.** Wind River formation. Black, soft, bituminous, clayey material. Taken from cored material. This layer is 21 feet thick, and the average U₃O₈ content was 0.12 per cent.

**GHLM-4 - Lucky Mac Mine.** Wind River formation. Dark grey mudstone. A lens in the typical sands but stratigraphically above samples GHLM-1 and 2. Counts 0.15 mr/hr. Not ore.

**GHLM-5 - Lucky Mac Mine.** Wind River formation. Selenium "ore" in typical sandstone. According to the Trace Elements Section of the Atomic Energy Commission, this red material is native selenium. The mine operator claimed that some ore ran 2.7 per cent selenium.
GHLM-6 - Lucky Mac Mine. Wind River formation. Good primary ore in typical sandstone. Small stringers of secondary material noted which according to E. Grutt was liebigite. Counts 5.0 mr/hr.

GHLM-7 - Lucky Mac Mine. Wind River formation. Typical grey, conglomeratic grit. Includes part of a carbonaceous ledge 1/2-inch thick. Not ore.

GHLM-8 - Lucky Mac Mine. Wind River formation. Grey, unoxidized, pyritic, calcareous grit. Part of a remnant boulder measuring about four by three by two feet. Sample taken from near edge. These bodies are rather common throughout the oxidized sands.

GHC-9 - Cochan Mine. Upper and middle Eocene beds. Richly bituminous grit from ore stockpile. Counts 0.5 mr/hr.

GHC-10 - Cochan Mine. Same as GHC-9 except this sample contains black lustrous tar.

GHC-11. Same as GHC-9 except highest count for ore in stockpile was 2.0 mr/hr.

GHC-12 - Cochan Mine. Blue calcareous claystone and grit which underlie present ore horizon. Operator states that all the ore is underlain by similar rock.

GHC-13 - Cochan Mine. Bituminous grit exposed by latest shooting in ore body. Highest count for ore exposed was 5.0 mr/hr.

GHC-14 - Cochan Mine. Calcareous grit below a bituminous layer which is probably the same horizon as GHC-13. Face from which sample was taken has only slight count above background.

GHW-15. Spring water, sulfurous with slow bubbling of gas through water. Spring 3 feet in diameter by 18 inches deep. Good flow of water, perhaps 5-10 gallons per minute. Inflow is so vigorous that 4 or 5 small shale-particle fountains 3 or 4 inches high have formed. Spring is located about 3 miles east of Cochan Mine in the Conant Creek anticline near the Chugwater-Phosphoria contact of the east flank. Beds strike N 30° W with a dip of 45° E. This location is about 1/4-1/2 mile south of the point where the Chugwater plunges beneath the surface.

GH-16. Black mud from spring of GW-15, from underwater.
GH-17. Dirt from within 8 feet of spring of GHW-15.


GH-21. Gas Hills Seep. Black, soft asphaltic material within 3 or 4 feet of GHG-18. This material is abundant but irregularly deposited around seep. Compares with GH-19 and GHLM-3.


GHV-24. Vitro Mine. Wind River formation. Ore sand or grit, black, soft and friable. E. Grutt of the Atomic Energy Commission says this kind of ore runs 8-10 per cent U₃O₈. Counts 5.0 mr/hr.

GHV-25. Vitro Mine. Grey grit taken near drop cut about 60 yards from GHV-24. This sample was to represent typical unoxidized and unmineralized Wind River sandstone; however, it had a count of 0.6 mr/hr.

GH-26. Supposedly normal unaffected grit of the Wind River formation that constitutes the ore where mineralized. Very low count. The rock is cross-bedded, conglomeratic, argillaceous and feldspathic. It is found about a mile N 72° W from Vitro Mine.

Treatment of Samples

On October 27, 1955, in a meeting between Messrs. Towle and Grutt of the Atomic Energy Commission and Messrs. Igel and Smith of the Research Foundation, it was decided that each of the above samples would be treated as follows:
Key:  AEC - Atomic Energy Commission
      CSMRF - Colorado School of Mines Research Foundation
      cU - Chemical Uranium Analysis
      eU - Radiometric Uranium Analysis

GHLM-1 Spectrographic analysis by AEC.
       Micro-comparison with GH-26 by CSMRF.

GHLM-2 Spectrographic analysis by AEC.
       Micro-comparison with GH-26 by CSMRF.

GHLM-3 Spectrographic analysis by AEC.
       eU and cU by AEC.

GHLM-4 Spectrographic analysis by AEC.
       eU and cU by AEC.

GHLM-5 Hold for consideration of Se influence.

GHLM-6 Hold for typical material and for decision by CSMRF.

GHLM-7 Split and hold.
       eU and cU by AEC.

GHLM-8 Spectrographic analysis by AEC.
       eU and cU by AEC.
       Total S by CSMRF.

GHC-9, 10, 11, 12, 13, and 14 Hold for Lucky Mac results.

GHW-15 Spectrographic analysis by CSMRF.
       Total As, S, Se, and $P_2O_5$ by CSMRF.


GH-17 Hold for later decision.

GHG-18 Gas analysis by CSMRF.

GH-19 Spectrographic analysis by AEC.

GHW-20 Spectrographic analysis by CSMRF.
       Total As, S, Se, and $P_2O_5$ by CSMRF.
GH-21, 22, and 23 Spectrographic analysis by AEC. Total S and asphalt by AEC. Determination of fine black material by CSMRF. Compare this black material with black lustrous material of Samples GHLM-3, GHC-10, and GH-19 by CSMRF.

GHV-24 Spectrographic analysis by AEC. eU and cU by AEC. V₂O₅ by AEC. Total S by AEC. Total Fe by CSMRF.

GHV-25 Hold.

GH-26 Fluorimetric U and complete spectrographic analysis by AEC.

Results of Analyses

The results of the spectrographic, chemical and radiometric analyses are summarized in Table I, Appendix.

X-Ray Diffraction Method of Analysis

Determination of the presence of uraninite by X-ray diffraction is a positive method; it is not, however, sufficiently sensitive to identify trace minerals. Table II in the Appendix shows a typical diffraction pattern analysis compared to a standard pattern for uraninite (UO₂). This comparison gives an indication of how positive this method of identification can be.
THEORETICAL CONSIDERATIONS(1)

If we assume that the uranium is transported to the ore body as hexavalent uranium in solution, then some reducing agent is present. This reducing agent must be powerful enough to carry out the reduction of the hexavalent uranium to tetravalent uranium under the conditions existing at the time of formation of the ore. The hexavalent uranium was presumably dissolved in water at high temperatures, possibly as high as 200° C.

Unfortunately, sufficient thermodynamic data are not available to make exact calculations possible, especially for elevated temperatures. However, good qualitative results can be obtained.

Ferrous ion is present in the waters near the ore, as shown by the presence of FeS. Since Fe^{++} is a fair reducing agent, it may be the substance which reduces the U^{+6} to U^{+4}, according to the following equation:

\[
\text{UO}_2\text{SO}_4 + 2\text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{UO}_2
\]

(1)

If 6.302 grams of UO_2SO_4·3H_2O is treated with 0.178 gram of FeSO_4·7H_2O it is possible to convert 2.1 per cent of the uranium to UO_2, if the reaction were to go to completion. However, thermodynamic calculations indicate that the reaction is not possible.


1/ Written by Dr. R. Thomas Myers, Chemistry Department, Colorado School of Mines.
\[ 2\text{Fe}^{++} = 2\text{Fe}^{+++} + 2e^{-} \quad \text{E}^{\circ} = -0.77 \text{ volt} \quad (2) \]

\[ \text{UO}_2^{++} + 4\text{H}^+ + 2e = \text{U}^{+4} + 2\text{H}_2\text{O} \quad \text{E}^{\circ} = 0.33 \text{ volt} \quad (3) \]

\[ \text{UO}_2^{++} + 2\text{Fe}^{++} + 4\text{H}^+ = \text{U}^{+4} + 2\text{Fe}^{+++} + 2\text{H}_2\text{O} \quad \text{E}^{\circ} = -0.44 \text{ volt} \quad (4) \]

From the equations

\[ \Delta F^{\circ} = -nF\text{E}^{\circ} = -RT\ln K \quad (5) \]

we can calculate for reaction (4) an equilibrium constant of \(1.2 \times 10^{-15}\) at 25\(^\circ\) C.

\[ \frac{A_{\text{U}^{+4}} \cdot A^{2}_{\text{Fe}^{+++}}}{A_{\text{UO}_2^{++}} \cdot A^{2}_{\text{Fe}^{++}} \cdot A^{4}_{\text{H}^+}} = 1.2 \times 10^{-15} \quad (6) \]

If one assumes that the actual molar concentrations are equal to activities, then one can calculate the concentration of \(\text{U}^{+4}\) at equilibrium at a pH of 1 (6.302 grams \(\text{UO}_2\text{SO}_4\cdot3\text{H}_2\text{O}\) and 0.178 gram of \(\text{FeSO}_4\cdot7\text{H}_2\text{O}\) in 30 milliliters of water). The result is \(1.6 \times 10^{-8}\) moles per liter.

The \(\text{U}^{+4}\) is converted to \(\text{UO}_2\) by the following reactions:

\[ \text{U}^{+4} + \text{H}_2\text{O} = \text{UO}^{++} + 2\text{H}^+ \quad (7) \]

\[ \text{UO}^{+2} + \text{H}_2\text{O} = \text{UO}_2 + 2\text{H}^+ \quad (8) \]

Considering that the reactions are reversed by the presence of \(\text{H}^+\), it is not to be expected that \(\text{UO}_2\) will be formed in high enough concentration to precipitate from solution at pH 1.

There is insufficient data to predict the effect of temperature on the reactions above.
If, however, \( \text{H}_2\text{S} \) is examined as a possible reductant, the situation is quite favorable. The reaction is as follows:

\[
\text{H}_2\text{S} + 4\text{UO}_2^{++} + 8\text{H}^+ = \text{H}_2\text{SO}_4 + 4\text{U}^{++} + 4\text{H}_2\text{O}
\]  

(9)

Data from the book by Latimer give a standard free energy change of -5,560 calories for this reaction. Calculation by equation (5) gives an equilibrium constant of \( 8 \times 10^4 \).

\[
\frac{\text{A}_{\text{H}_2\text{SO}_4} \cdot \text{A}_{\text{U}^4}^4}{\text{A}_{\text{H}_2\text{S}} \cdot \text{A}_{\text{UO}_2^{++}}^4 \cdot \text{A}_{\text{H}^+}^8} = 8 \times 10^4
\]

(10)

This means that if a solution saturated with \( \text{H}_2\text{S} \) at 25° C (about 0.1 molar) is reacted with 0.1 molar \( \text{UO}_2^{++} \), the resultant reaction mixture would contain \( \text{U}^{++} \) at a concentration of about 0.007 molar (assuming activities and molarities to be the same). Since \( \text{UO}_2 \) is a very insoluble substance one would expect it to be precipitated by reactions (7) and (8).

It should be noted that equation (9) is shifted to the left at higher pH, and that equations (7) and (8) are shifted to the right. This would indicate that the previous calculations would hold approximately at a pH of 6.

Another possible reaction is even more favorable thermodynamically.

\[
\text{H}_2\text{S} + \text{UO}_2^{++} + 2\text{H}^+ \rightarrow \text{S} + \text{U}^{+++} + 2\text{H}_2\text{O}
\]

(11)

The standard free energy change is -8,840 calories, giving an equilibrium constant of \( 2.6 \times 10^8 \). If a 0.1 molar solution of \( \text{H}_2\text{S} \) is reacted with a 0.1 molar solution of \( \text{UO}_2^{++} \), 99 per cent of the \( \text{UO}_2^{++} \) is converted to \( \text{U}^{++} \).

Combination of equations (7) (8) and (11), or (7) (8) and (9), show that the solution becomes more acidic as the reaction proceeds.
To summarize: (1) Iron as ferrous ion is not able to reduce hexavalent uranium to the tetravalent state. (2) Hydrogen sulfide is a much better reductant, and can accomplish this reduction.
EXPERIMENTAL WORK

Experimental Techniques

Preparation of Salts

The first step in the experimental work was the preparation of water-soluble uranium salts. A typical ore sample, GHLM-6, from the Lucky Mac Mine of the Gas Hills Area was chosen. The mineralogical composition of Lucky Mac Ore is given in Table III, Appendix.

The sample, GHLM-6, was crushed and pulverized so that all the material would pass a 100-mesh (Tyler) screen. The following splits were made:

Part I 1257 grams (for first experiments)
Part II 1160 grams (for later experiments)
Part III 73 grams (for possible later assay)
In addition two hand specimens were reserved.

Concentrated sulfuric acid was added to Part I which completely wetted the crushed ore to make a thick paste. This paste was then placed on a gas stove to drive off excess sulfuric acid. The dried paste was mixed with 4000 milliliters of distilled water and vacuum filtered. The resultant solution was light green to yellow in color and presumably carried the quadrivalent and hexavalent ions of uranium. Fifty cubic centimeters of this solution were set aside and designated Solution "A." The remainder of the solution was placed on a gas stove. After all water had been evaporated, uranyl and uranous sulfates, as well as other salts, remained. These salts were then split. The first portion was ground and designated Salt "A."
The second portion was mixed again with 1000 milliliters of distilled water. Sufficient hydrogen peroxide was added to oxidize all uranium to the hexavalent state. This solution, now yellow-orange in color, was evaporated. The resultant salts were ground and designated Salt "B."

One-quarter pound of uranyl acetate powder, \(\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}\), was dissolved in concentrated sulfuric acid. This solution was placed on a gas stove to remove the sulfuric acid. A reduced green salt, uranium sulfate \((\text{U(SO}_4)_2 \cdot 4\text{H}_2\text{O})\), was formed. This salt was dissolved in 1000 milliliters of distilled water and then was oxidized to hexavalent uranium by the addition of hydrogen peroxide. The water was evaporated, and the uranyl sulfate salt, \(\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}\), was obtained. This salt was designated Salt "C."

**Preparation of Solutions**

By definition, a one molar uranyl sulfate solution contains 420.184 grams of uranyl sulfate in 1000 grams of water. A 0.5 molar uranyl sulfate \((\text{UO}_2\text{SO}_4)\) solution was arbitrarily chosen for the experimental work. A 0.5 molality is equivalent to 210.093 grams of \(\text{UO}_2\text{SO}_4\) in 1000 grams of water or 6.302 grams \(\text{UO}_2\text{SO}_4\) in 30 grams of water or 4.201 grams \(\text{UO}_2\text{SO}_4\) in 20 grams of water.

The desired uranium to iron ratio for the tests was calculated on the following basis:

\[
\frac{\text{U}}{\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}} = \frac{238.07}{420.184} = 0.5666
\]

Therefore, 6.302 grams of uranyl sulfate contains 6.302 x 0.5666 or 3.569
grams of uranium. If a uranium to iron ratio of 100 to 1 is desired then
0.01 x 3.569 or 0.03569 gram of iron are needed. If the iron is in the form of ferrous sulfate (FeSO₄·7H₂O) then:

\[ \frac{Fe}{FeSO₄·7H₂O} = \frac{55.85}{278.02} = 0.2009 \]

Therefore, 0.03569/0.2009 or 0.1778 gram of ferrous sulfate will contain 0.0369 gram of iron, which is the necessary amount to give a uranium to iron ratio of 100 to 1.

Similar computations were made for each different source of iron used as well as for other uranium to iron ratios.

The solutions were prepared by weighing out the desired amounts of uranyl sulfate, ferrous salts, and water on a Gram-matic Analytical Scale accurate to 0.0001 gram.

The pH measurements were made before and after the tests with a standard Model H-2 Beckman pH Meter with glass electrode.

**Method of Recovery of UO₂**

**Qualitative--**After subjecting the salt solutions to the various desired tests, the reaction tube containing the digested solution was opened and the solution was carefully decanted into a filter paper which retained the small particles of UO₂. The pH of the filtrate was measured and reported as the final pH. The filter paper was washed three times with distilled water to remove any uranyl sulfate solution. The filter paper was allowed to dry at ambient temperatures for two days. The residue was collected for uranium analysis by either spectrographic or X-ray diffraction methods.
Quantitative—For quantitative analysis in order to obtain maximum accuracy in measuring the amount of uraninite precipitate, the need was realized for a method of high inherent sensitivity. Such a method is obtained by the use of fine porosity glass filters. The procedure was as follows:

The glass filter was very carefully weighed while empty and dry. All weighings were on a Gram-matic Analytical Scale which is accurate to 0.0001 gram.

The solution was filtered through the fine porosity glass which traps all the uraninite on the filter. The precipitate was washed with distilled water to remove any traces of soluble salts. The filter and uraninite were dried in a desiccator for a minimum of eight hours.

The glass filter containing the uraninite was again very carefully weighed.

The tare weight of the glass filter was then subtracted from the gross weight.

**Calculation of Percentage Yield**

The available uranium in the original solution was:

\[ \frac{U}{UO_2SO_4 \cdot 3H_2O} = \frac{238.07}{420.184} = \frac{A}{B}, \text{ therefore, } A = 0.5666B \]

where:  
A is the available uranium in solution in grams.  
B is the uranyl sulfate in solution in grams.

The amount of uranium in the \( UO_2 \) precipitate is:

\[ \frac{U}{UO_2} = \frac{238.07}{270.07} = \frac{C}{D}, \text{ therefore, } C = 0.8815D \]

where:  
C is the amount of uranium in grams.  
D is the amount of uraninite in grams.

The yield of uranium in per cent of available uranium is equal to:

\[ \text{Yield of } U = \frac{100C}{A} = \frac{88.15D}{0.5666B} = \frac{155.577 \times \text{Weight of } UO_2}{\text{Weight of } UO_2SO_4 \cdot 3H_2O} \]
Proof of the Presence of Ferrous Sulfide in Sample GH-19

Interest was shown in Sample GH-19 since it is so intimately associated with GHG-18 and GHW-20. GH-19 as found in the native state is a black amorphous material. Upon exposure to air it rapidly changes to a light brownish-grey color and appears to be a typical silt. Minerals present are: quartz, major; calcite, minor; feldspar, minor; and mica, minor.

X-ray diffraction analysis of this material in its original state showed the presence of the following: quartz, montmorillonite, feldspar, and calcite. The detection limit of X-ray diffraction is low, thus any substance present in an amount less than five per cent of the total would not be identified.

On the assumption that the black material might be organic, a sample was analyzed for moisture content, loss on ignition, and total carbon content. The results were:

<table>
<thead>
<tr>
<th>Moisture (%)</th>
<th>Loss on Ignition (%)</th>
<th>Total Carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>6.53</td>
<td>2.06</td>
</tr>
</tbody>
</table>

The GH-19 material exhibited some rather characteristic properties in that as it was dried this material changed from a black amorphous material to brownish-grey silt. If the dried material were again wetted and hydrogen sulfide was percolated through it, the sample again became black amorphous material. This procedure could be repeated many times with the same result.
A 10-gram sample of GH-19 in its original state was leached with concentrated hydrochloric acid. This gave a highly effervescent reaction with a strong odor of hydrogen sulfide.

The residue from filtering, even though wet, closely resembled the dried GH-19, which appeared to be brownish-grey silt. This residue and the same amount of dried GH-19 were placed in separate beakers. Duplicate amounts of distilled water were added to each beaker. The appearance of the two mixtures was identical at this point. Hydrogen sulfide gas was then bubbled through each solution simultaneously. The sample of dried GH-19 gave a black precipitate which coated the entire mass. The sample containing the leached residue did not change. Thus, whatever had caused the color change had been leached from the sample and was in the filtrate left after leaching.

The filtrate from leaching was a clear yellow liquid with a pH of 0.8. A portion was tested for copper. The results were negative.

The remainder of the filtrate was neutralized by the addition of sodium hydroxide. A dark-green precipitate was formed as the solution became basic. If ammonium, sodium, or potassium hydroxide is added to a neutral solution containing ferrous iron, gelatinous precipitate of ferrous hydroxide \( \text{Fe(OH)}_2 \), is formed which on exposure to air is rapidly oxidized, becoming first dirty-green, then black, and finally reddish-brown. The equations for this reaction are:
\[
\text{Fe}^{++} + 2 \text{(OH)}^- \rightleftharpoons \text{Fe(OH)}_2
\]

and

\[
4 \text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4 \text{Fe(OH)}_3
\]

The GH-19 solution was again acidified and the precipitate redissolved. A few drops of ammonium thiocyanate were added to a sample of this solution. The solution turned a deep blood red which proved qualitatively the presence of iron.

Hydrogen sulfide was bubbled through the other portion of the sample. A heavy black precipitate was formed. This reaction follows the equation:

\[
\text{Fe}^{++} + \text{H}_2\text{S} \rightleftharpoons \text{FeS} + 2\text{H}^+
\]

This indicates that the black mineral in GH-19 is ferrous sulfide. It is formed in nature by the hydrogen sulfide gas bubbling up through iron-bearing solutions.

**Experimental Conditions**

From the preliminary studies, the decision was made to use uranyl sulfate and ferrous ions in the laboratory work. Uranyl sulfate probably occurs in nature associated with the ferrous ions which are known to be present. Natural gas, natural gas with hydrogen sulfide content removed (desulfurized), helium, hydrogen sulfide, hydrogen, and air were to be used as the experimental atmospheres. The discussion of the individual experiments will show which gases were used and the method of establishing the desired atmosphere.
Preliminary Experiments

Preliminary Experiment

The first experiment was designed to determine whether natural gas would act as a reducing or a precipitating agent on Solution "A." Methyl orange indicator was added to Solution "A," and calcium carbonate was added to increase the pH of the solution to 4.1. The resultant calcium sulfate precipitate was removed by vacuum filtration. The uranium concentration of the solution was unknown, but a positive lithium-sodium fluoride bead test indicated the presence of uranium in solution. This solution, approximately 50 cubic centimeters, was poured into a gas absorption bottle to which heat was applied. Natural gas as received from city lines was bubbled through the solution while the temperature was held between 93 and 96° C. This process was continued for approximately 40 hours at the end of which time distilled water was added to bring the solution to its original volume; the pH was now 2.3. The color of the solution was light green. A small amount of precipitate, the major part of which was calcium sulfate, had formed. A very small amount of dark opaque material was seen in this precipitate. This solution was set aside at room temperature, and after four weeks a larger quantity of the dark opaque material was present. An attempt to recover the minute quantity of dark material failed and all the material was lost.

Autoclave Experiments

For this work the standard one-liter Magne-Dash Autoclave, manufactured by Autoclave Engineers, Inc., was used.
The autoclave is essentially a steel cylinder having a metal pressure gasket and threaded cap. This apparatus also incorporates the following features: a thermocouple well, pressure-gage connection, three gas connection and sampling tubes, safety head rupture disk, magnetically-driven agitation element of reciprocating motion, and an external 2000-watt heating element. Temperature recording and control is achieved by the use of a Wheelco Capacilog Scriber, manufactured by Wheelco Instruments Company.

The experiments to date have all been made in this equipment.

Experiment No. 1

The purpose of Experiment No. 1 was to check whether hydrogen sulfide would precipitate uraninite from an aqueous solution of uranyl sulfate and ferrous sulfate as stated by John Gruner. In addition, this experiment would afford the opportunity to develop necessary techniques of handling and mixing solutions and also to check the operation of the autoclave.

The solution contained 30 grams of distilled water; 6.302 grams of uranyl sulfate, Salt "C"; and 0.178 grams of ferrous sulfate, FeSO$_4$·7H$_2$O. The pH of the solution was 1.1 when it was placed in a 65-cubic-centimeter reaction tube. Hydrogen sulfide was bubbled through the solution for ten minutes. A large quantity of free sulfur was now present in solution. The tube was then capped with a rubber gasket and a bakelite screw cap and placed in the autoclave. Before sealing the autoclave, 400 cubic centimeters of water were added to equalize the subsequent high vapor pressure within the
reaction tube that would result upon the application of heat to the system.

The following autoclave temperatures and pressures were recorded:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure pounds per square inch (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>177</td>
<td>150</td>
</tr>
<tr>
<td>182</td>
<td>170</td>
</tr>
<tr>
<td>188</td>
<td>200</td>
</tr>
<tr>
<td>199</td>
<td>250</td>
</tr>
<tr>
<td>200</td>
<td>245</td>
</tr>
<tr>
<td>205</td>
<td>275</td>
</tr>
</tbody>
</table>

Essentially these same temperatures and pressures acted on the reaction tube. The temperature control level was set at 200° C (392° F). There was some "over and under-shoot" in temperature, range 20° C, and corresponding pressure; but the average temperature of the reaction tube was 200° C and the average pressure was 250 psi. The retention time was arbitrarily set for 88 hours. Unfortunately, the autoclave was inoperative for some undefined period, and it is known only that the retention time was greater than 44 hours and less than 88 hours. Upon opening the autoclave and recovering the reaction tube it was found that the rubber gasket and bakelite cap had deteriorated. New gasketing material, an asbestos, cord-reinforced, heat-resistant rubber, was found; however, it is felt that the bakelite caps must be discarded after each test run.

The following is a physical description of the precipitate:

85 per cent of the precipitate was black material which formed in small spherical grains. There were larger black masses that appeared to form in flattened crystalline plates. 8 per cent was colorless rectangular crystals.
that appeared to be orthorhombic. The material was anisotropic with parallel extinction, biaxial, moderate birefringence, and had a range of index of refraction of 1.54 to 1.62. 7 per cent was yellow-brown material of limonite color which coated all other materials. A spectroscopic examination revealed the following: uranium, strong; magnesium, weak; iron, weak.

The solution present in the reaction tube was decanted. No free sulfur was present. The pH of the solution was 0.5. Gruner explains the disappearance of the sulfur and the increase in hydrogen ion concentration by the following equations:

\[
\begin{align*}
\text{UO}_2^{++} + 2\text{Fe}^{++} & \rightarrow \text{U}^{++++} + 2\text{Fe}^{+++} + 20^= \\
& \quad \downarrow \quad \downarrow \\
& \quad 2\text{Fe}^{++} + \text{S}^0 + 2\text{H}_2\text{O} \\
& \rightarrow \text{U}^{++++} \\
4\text{H}_2\text{O} & \leftarrow 4(\text{OH}^-) + 4\text{H}^+ \\
& \downarrow \\
\text{U(OH)}_4 & \rightarrow \text{UO}_2 + 2\text{H}_2\text{O} \\
\text{U(SO}_4)_2 & \rightarrow \text{UO}_2 + 2\text{SO}_3 \\
\text{SO}_3 + \text{SO}_4^= & \rightarrow \text{S}_2\text{O}_7^= \\
\text{S}_2\text{O}_7^= + \text{S}^0 & \rightarrow \text{S}_3\text{O}_7^= \\
2\text{S}_3\text{O}_7^= & \rightarrow \text{S}_2\text{O}_3^= + \text{SO}_4^=
\end{align*}
\]
The precipitate from this experiment was radioactive. Its X-ray diffraction pattern gave pure uraninite as shown by comparison of "d" spacing values in Table II in the Appendix.

**Experiment No. 2**

The purpose of Experiment No. 2 was to determine whether natural gas from the city lines (see Table I, Appendix) would precipitate uraninite from an aqueous solution of uranyl sulfate and ferrous sulfate.

The solution was identical to the solution used for Experiment No. 1 except that the pH was 1.0 instead of 1.1. Natural gas was bubbled through the solution for approximately ten minutes, and the tube was capped. No change in the solution's appearance was evident after passing the natural gas through it.

Experiment Nos. 1 and 2 were digested simultaneously. Consequently, the retention time for No. 2 was likewise greater than 44 hours and less than 88 hours.

The following is a physical description of the precipitate from Experiment No. 2:

10 per cent of the precipitate was black material which formed in small spherical grains; 25 per cent was black material that appeared to form in flattened, crystalline plates; 50 per cent was the same rectangular, colorless crystals described in the results of Experiment No. 1; 15 per cent was reddish-brown material of hematite-like color which coated all other materials in the precipitate.
A spectroscopic examination revealed the following: uranium, weak (less than Experiment No. 1); magnesium, medium (more than Experiment No. 1); iron, medium (more than Experiment No. 1); potassium, weak; sodium, weak.

The solution present in the reaction tube was yellow in color. No free sulfur was apparent. The pH was 0.7.

The precipitate from this experiment was radioactive. The X-ray diffraction pattern showed the presence of uraninite. The total amount of precipitate present in Experiment No. 1, however, was about 10 times greater than that of Experiment No. 2.

**Experiment No. 3**

This experiment was identical to No. 1 and was made to check the results of Experiment No. 1. The pH of original solution was 0.9. The retention time was greater than 3 hours and less than 72 hours. It is significant that a reaction did take place. The pH of the solution after the reaction was 0.7. The precipitate was uraninite.

**Experiment No. 4**

Experiment No. 4 was made to determine whether or not the hydrogen sulfide that was perhaps present in the city gas was responsible for the results of Experiment No. 2.

Gas from the city mains was desulfurized by bubbling through a slightly acidic solution of copper sulfate before being bubbled through the uranium solution. The experiment was otherwise identical to Experiment No. 2. It was run at the same time as Experiment No. 3.
The pH of the solution after digestion was 0.8. A precipitate was formed which was very similar to the precipitate formed in Experiment No. 2.

**Experiment No. 5**

Experiment No. 5 was made to see what effect air had on the precipitation of uranium. Some of the same solution used in the first four experiments was placed in a reaction tube. Air was bubbled through the solution to saturation. The tube was placed in the autoclave.

The original pH of the solution was 0.9. The pH after digestion was 0.8. A precipitate was formed. There is some question as to whether the atmosphere in Experiment Nos. 4 and 5 was contaminated.

These preliminary experiments in the autoclave are summarized in Table IV, Appendix.

**Discussion**

Precipitates formed in Experiment Nos. 1 and 2 definitely contained uraninite. Uraninite is essentially a mixture of uranous (UO₂) and uranic (UO₃) oxides. In newly formed material it is believed that UO₂ is predominant and by oxidation UO₂ changes to UO₃.

Experiment Nos. 4 and 5 were for the purpose of determining whether natural gas, principally methane, had an effect on the precipitation of uraninite from uranium solutions. It was not established whether desulfurized natural gas had any more effect than air on the precipitation of uraninite. However, hydrogen sulfide precipitated more uraninite from solution than did either natural gas or air.
It is interesting to note that in the autoclave experiments a uraninite precipitate appeared to form at the gas-liquid interface and adhered to the periphery of the tube; the major part of the precipitate, however, was found at the bottom of the tube in a loose or unconglomerated state. It is probable that the reaction takes place only at the gas-liquid interface. This would imply that the quantity of uranium precipitated under set conditions and a given reaction time would depend upon the surface available at the interface. Geologically, this might be related to the porosity of the host rock.
Increased Temperature Experiments

Increased temperature experiments conducted in standard thermostatically-controlled drying ovens covered a range from 50 to 100° C. Since the temperatures were relatively low, the starting solutions were placed in 3-ounce wide-mouth jars with brass screw caps and paper gaskets. The temperature and retention time of all experiments, Nos. 6 through 11, were 85° C and 170 hours, respectively. All experiments, Nos. 7 through 11, were processed in this same manner as described for Experiment No. 6.

Experiment No. 6

The purpose of this experiment was to determine whether a hydrogen sulfide atmosphere would precipitate uraninite from an aqueous solution of Salt "A."

The solution contained 30 cubic centimeters of distilled water and 6.302 grams of Salt "A." The initial pH was 1.1. Hydrogen sulfide was bubbled through the solution for approximately ten minutes, and the jar was then capped and placed in an oven at 85° C. At the end of 170 hours, the jar was removed. A precipitate had formed. As most of the solute had evaporated, no final pH measurement was made. The precipitate was washed with distilled water and filtered. A second wash with dilute hydrochloric acid, 200 cubic centimeters of distilled water to 20 cubic centimeters of concentrated hydrochloric acid, was followed by filtration. The salt was then allowed to dry at room temperature.
The precipitate from this experiment was complex because of the original composition of Salt "A." The precipitate was radioactive and of secondary origin; no identification of the mineral was made. However, no uraninite was present.

Experiment No. 7

The purpose of this experiment was to determine whether uraninite would be precipitated from an aqueous solution of Salt "A" in the presence of an air atmosphere.

The solution contained 30 cubic centimeters of GHW-20 and 6.302 grams of Salt "A." The initial pH was 1.1. This solution was capped; no air was bubbled through the solution.

The precipitate contained no uraninite, but did contain another mineral that to date has not been identified.

Experiment No. 8

The purpose of this experiment was to determine whether an atmosphere of hydrogen sulfide and dried GH-19 in an aqueous solution of Salt "A" would precipitate uraninite.

The solution contained 30 cubic centimeters of distilled water, 6.302 grams of Salt "A", and approximately 1.0 gram of GH-19 that had been dried at room temperature. The initial pH was 1.2

The precipitate was a complex radioactive salt containing some dark, opaque material. X-ray diffraction analysis showed no uraninite present; however, it did show quartz and jarosite, \( \text{K Fe}_3(\text{SO}_4)_2(\text{OH})_6 \).
Experiment No. 9

This experiment was the same as Experiment No. 8 except for the processing of GH-19. Approximately 5 grams of GH-19 were dried at room temperature and 30 cubic centimeters of concentrated nitric acid were added. Six drops of perchloric acid were added to the solution, and the acid was subsequently evaporated by heating the solution on a hot plate. The recovered salts were now free of all carbon and carbonaceous material.

The precipitate showed a complex radioactive salt exhibiting some opaque material. X-ray diffraction analysis showed no uraninite present; however, it did show quartz and jarosite.

Experiment No. 10

The purpose of this experiment was to determine whether uraninite would be precipitated in an air atmosphere from an aqueous solution of Salt "A" with the addition of 1.0 gram of GH-19.

The solution contained 30 cubic centimeters of distilled water, 6.302 grams of Salt "A," and approximately 1.0 gram of unoxidized GH-19.

The precipitate was a complex salt which was radioactive. An X-ray diffraction analysis showed no uraninite present; however, it did show quartz and jarosite.

Experiment No. 11

The purpose of this experiment was to determine whether a natural gas atmosphere would precipitate uraninite from an aqueous solution of Salt "A."
The solution contained 30 cubic centimeters of distilled water and 6.302 grams of Salt "A." Natural gas, as received from the city lines, was bubbled through the solution for approximately ten minutes.

The precipitate from this experiment was radioactive. No identification of the mineral was made. No uraninite was present.

Experiment No. 12

The purpose of this experiment was to determine whether in a hydrogen sulfide atmosphere uraninite would be precipitated from an aqueous solution of uranyl sulfate and metallic lower valence ions.

The solution contained 3.151 grams of uranyl sulfate, Salt "C," and 30 cubic centimeters of distilled water containing the soluble salts from a 5-gram sample of dried GH-19. The solution was digested for three hours and filtered. The filtrate was added to the uranyl sulfate salts. The solution was placed in a 3-ounce wide-mouth jar, and hydrogen sulfide was bubbled through it for approximately ten minutes. The jar was then capped and placed in an oven which was thermostatically controlled at 100° C. After 24 hours the temperature within the oven had risen to 120° C and the solution had evaporated. Distilled water was added to the evaporated salts and a small amount of dark, water-insoluble, material, probably uraninite, was recovered.

Experiment No. 13

The purpose of this experiment was to determine whether in a desulfurized natural gas atmosphere, uraninite would be precipitated from an aqueous solution of uranyl sulfate and metallic plus-2-valance ions.
The solution was identical to that used in Experiment No. 12, and this experiment was run concurrently with Experiment No. 12. A small quantity, approximately a quarter of that from Experiment No. 12, of dark, water-insoluble salts was present.

Discussion

Work carried on in the increased temperature range, 50 to 100° C, indicated that at these temperatures the parameters, type of gas, catalytic agents, pH, etc., play an increasingly important role in the precipitation of uraninite; and, therefore, more of the variables associated with the problems must be explored. It is felt, however, if sufficient time were allowed, the same reactions would take place as occur under accelerated conditions. The results of Experiment Nos. 6 through 13 are summarized in Table V, Appendix.

Qualitative Autoclave Experiments

In the earlier autoclave experiments there was a question concerning the possibility of contamination because several reaction tubes which had different gaseous atmospheres were placed in the autoclave at one time. In addition, the atmosphere within the autoclave was air. To eliminate the possibility of contamination it was decided (1) to place a single reaction tube in the autoclave at one time and (2) to replace the air atmosphere within the autoclave with the same atmosphere that existed within the tube under investigation.

Experiment No. 14

The purpose of this experiment was: (1) To determine whether desulfurized natural gas would precipitate uraninite from an aqueous solution of
The purpose of this experiment was: (1) To determine whether in conjunction with a helium atmosphere uraninite would be precipitated from an uranyl sulfate and ferrous sulfate; and (2) to determine the percentage yield of uranium in the uraninite precipitate.

The autoclave used in the experiments conducted under accelerated conditions was the same as previously described.

The solution contained 6.302 grams of uranyl sulfate, Salt "C;" 0.178 gram of ferrous sulfate; and 30 grams of distilled water that had been boiled to remove the oxygen. This solution, pH 1.2, was placed in a reaction tube. Desulfurized natural gas was bubbled through the solution for approximately ten minutes. The tube was then capped with a heat-resistant, asbestos-filled rubber gasket and a bakelite screw cap.

Initially this tube was placed in an oven which was thermostatically-controlled at 100°C. The retention time in the oven was 48 hours. After this period of time the tube was examined. Some reaction was evidenced by a thin brownish-colored film at the liquid-gas interface.

The tube was then placed in the autoclave and was held at 200°C and 250 psi pressure for 48 hours. When the tube was examined, a dark black precipitate was seen at the periphery of the gas-liquid interface as well as at the bottom of the tube. The pH of the solution was 1.0.

An X-ray diffraction analysis showed the presence of uraninite; the yield of uranium was 4.8 per cent.

Experiment No. 15

The purpose of this experiment was: (1) To determine whether in conjunction with a helium atmosphere uraninite would be precipitated from an
aqueous solution of uranyl sulfate and ferrous sulfate; and (2) to determine the percentage yield of uranium.

The solution for this experiment was identical to that of Experiment No. 14 except that the original pH was 1.1. This tube received the same processing as that of Experiment No. 14. When the tube was removed from the autoclave, the pH of the filtrate was 1.3; and a dark black precipitate was noted at the periphery of the gas-liquid interface as well as at the bottom of the tube. Since the cap was loose, leakage in the system was probable.

An X-ray diffraction analysis showed the presence of uraninite; the yield of uranium was 7.4 per cent.

Experiment No. 16

The purpose of this experiment was: (1) To determine whether in an air atmosphere uraninite would be precipitated from an aqueous solution of uranyl sulfate and ferrous sulfate; and (2) to determine the percentage yield of uranium.

The solution for this experiment was identical to that of Experiment No. 14 except that the original pH was 1.1. This tube was also processed in an identical manner to that of Experiment No. 14. The retention time, however, was greater than 48 hours and less than 61 hours. Upon removing the reaction tube from the autoclave a dark black precipitate was seen at the gas-liquid interface as well as at the bottom of the tube. The pH of the filtrate was 1.1.
An X-ray diffraction analysis showed the presence of uraninite as well as other minerals which have not been identified to date. The percentage of uraninite in the precipitate, estimated from the density of the diffraction lines, was approximately 60 per cent. This, in turn, gives a uranium yield of 1.8 per cent. Leakage was again indicated.

Experiment Nos. 17A, 17B, 17C, and 17D

The purpose of this series of tests was to determine the effect of pH on yield. Ten grams of Salt "B," 0.178 gram of ferrous sulfate, and 30 cubic centimeters of boiled distilled water were used in each of the four parts of this experiment. The pH was adjusted by the use of Na₂CO₃.

The four tubes were placed in the autoclave, and the temperature was slowly raised to 200°C and the pressure to 250 psi. This pressure and temperature were maintained for a period of digestion in excess of 48 hours but less than 52 hours. During this time, tube "17D" broke and the contents were lost.

Results—No. 17A yielded 3.8489 grams of a yellowish-grey precipitate with very low radiation count.

No. 17B yielded 0.3689 gram of a reddish-brown precipitate, also with a low radiation count.

No. 17C yielded 0.7932 gram of a brownish-black precipitate which upon drying took on a reddish tinge. This also gave a low count.
Experiment No. 18

The purpose of this experiment was to determine the effect of pH on the precipitation of uraninite from an aqueous solution if other variables were held constant.

Preparation of Samples--6. 302 grams of uranyl sulfate (Salt "C") were added to each of three beakers containing 30 cubic centimeters of boiled, distilled water. Because of the hydrolysis of the sulfate ion, the solution became acidic as the uranyl sulfate dissolved. The normal pH at this point was 1.3 to 1.4. By the addition of a small amount of H₂SO₄, the pH of "18A" was lowered to 1.0. To solution "18B" was added sodium carbonate (Na₂CO₃) in small amounts until the pH was 3.0. The solution had a slightly darker appearance but no precipitate was formed even with the application of heat. Solution "18C" was to have had a pH of 6.5 which was not possible to achieve because of heavy precipitation.

Further experimentation showed that any uranyl sulfate solution of this molality at a pH above 3.0 formed a precipitate. Therefore, a pH of 3.0 was taken as the upper limit at which precipitation did not occur.

Experiment No. 19

The purpose of this experiment was to determine whether or not UO₂ could be precipitated from an aqueous solution of UO₂⁺⁺ ions in the presence of chloride ions.
The solution was prepared by dissolving 10 grams of uranyl acetate in 200 cubic centimeters of water. The solution was heated in order to dissolve the powder completely. After cooling, 50 cubic centimeters of ammonium hydroxide were added to precipitate a diammonium uranate. This is a standard quantitative test, and it is believed that in an excess of ammonium hydroxide all of the uranium in the original ten grams was precipitated. This precipitate was then filtered and washed. It was then redissolved in dilute hydrochloric acid to a volume of 30 cubic centimeters. The pH was adjusted to 1.1.

As there was no commercially-prepared ferrous chloride available, it was prepared by the reaction of hydrochloric acid on iron filings:

\[
\text{Fe + 2HCl} \rightarrow \text{FeCl}_2 + \text{H}_2 \uparrow
\]

To obtain ferrous chloride (FeCl₂) as a dry powder is almost impossible. Therefore, a wet weight of 0.151 gram had to be used instead of the calculated 0.137 gram. However, it is believed that the ratio of uranium to iron was reasonably close to the desired 100 to 1.

Desulfurized natural gas was percolated through the solution for 10 minutes. The sample was then placed in the autoclave with a natural gas atmosphere at 200° C and 250 psi.

The tube was removed from autoclave after a digestion period of more than 48 hours but less than 52 hours. The amount of solution in the tube had increased from 30 to 41.0 cubic centimeters. The cap was slightly loose. An
appreciable amount of black precipitate had formed, apparently at the gas-
water interface, and had settled to the bottom of the tube. Some sooty black
substance had formed on the exterior of the tube and along the sides of the auto-
clave. This material had a radiation count of 0.6 mr/hr against a background
of 0.2 mr/hr. The precipitate formed inside the tube had a radiation count of
6.5 mr/hr. This was presumably UO₂.

The yield in per cent uranium to available uranium was approximately
26 per cent. The total yield was 0.434 gram from a solution containing 10
grams of uranyl acetate.

An X-ray analysis of samples from both inside and outside of the tube
showed that both were predominantly uraninite. The yield of uranium, there-
fore, is much higher than the calculated 6.96 per cent. The actual amount of
sooty UO₂ coating the outside of the tube and the interior of the autoclave was
probably 2 to 3 times the amount inside the tube.

Discussion

The results of Experiment Nos. 14 through 19 are summarized in
Table VI. These experiments, although qualitative, show definitely which
reactions can be expected. The comparative amounts of yield also give an
indication of the influence and importance of the variables.

Experiment No. 15 in which a helium atmosphere was used seems to
indicate that an inert could give as high or higher yield than the active gases.
This was later proved to be false. There was very good chance of contamina-
tion in this test, and it is felt that this probably caused the high yield. The
other experiments showed that the pH of the initial solution had a slight effect, and that the substitution of the chloride ion for the sulfate radical had only a negligible effect on the reaction.
Quantitative Autoclave Experiments

In all of the elevated temperature and pressure experiments prior to Experiment No. 21, it was assumed that the pressures inside and outside the tubes in the autoclave were approximately equal. Experimentally, this proved to be a false assumption since in every test the caps became loose and the solutions could escape. The amount of solution remaining in the tube in most tests varied widely from the starting amount. The tests were, therefore, only qualitative. Several possible solutions to this problem were studied.

A high-pressure glass bomb was designed for use outside the autoclave. The glass would withstand pressures up to 400 psi without breaking. However, there was no effective way to seal the bomb to prevent leakage.

The next approach to this problem was to seal a tube completely and place it in the autoclave. A thin-walled glass vial was first tried. The vial had a thin neck that was sealed under flame so that no leakage was possible. The vial was then placed in the autoclave under normal operating conditions. When it was removed after 48 hours, the vial had shattered.

Thick-walled pyrex glass tubes with long narrow necks were designed. This type tube can withstand some variation in pressure and can be sealed completely by the application of heat to the neck. The procedure for the preparation of solutions was to place the solution in the tube through the neck, pass a smaller tube inside the tube to bubble in the desired atmosphere, and then quickly to flame seal the neck with an oxygen-gas flame. Upon
completion of the tests the contents could be removed by scoring the neck with a file and snapping off the sealed end. This procedure proved to be satisfactory.

A glass filter crucible was used for the recovery of the precipitate.

**Experiment No. 22**

The purpose of this test was to confirm results of Experiment No. 15 in which a helium atmosphere was used and at the same time to vary the uranium to iron ratio to determine its effect on the per cent yield.

Three of the new pressure reaction tubes were used for these tests (Experiment Nos. 22A, B, and C). Into each tube was placed 20 cubic centimeters of solution containing 4.201 grams of uranyl sulfate. To one tube was added 0.2373 gram of FeSO₄ · 7H₂O which gave a uranium to iron ratio of 50 to 1. To the second tube was added 1.187 gram FeSO₄ · 7H₂O which gave a uranium to iron ratio of 10 to 1. To the third tube was added 11.870 grams of FeSO₄ · 7H₂O which gave a uranium to iron ratio of 1 to 1. The uranium sulfate molality was 0.5. Helium was then bubbled through the solutions. The tubes were sealed and placed in the autoclave to undergo a 48-hour digestion period at 200° C and 250 psi.

The fact that there was no precipitation with the helium atmosphere leads us to believe that previous experiments were contaminated by leaking systems. In the tube containing the 1 to 1 ratio of uranium to iron there was a heavy precipitation of white (presumably ferric) salts which masked the yield of UO₂.
Experiment No. 23

The purpose of this experiment was again to check results of Experiment No. 16 and also those of Experiment Nos. 22A and B and to check comparative yields with three different atmospheres.

The test was set up in three glass pressure tubes which were sealed and placed in the autoclave. All three solutions were identical except for the atmosphere used. All three were placed in the autoclave simultaneously so that all were subjected to the same conditions during the entire run. Variation in yield should then reflect the effect of the atmosphere present.

Results--23A (He atmosphere). Only a trace of precipitation appeared in the tube. This result corresponded to that of Experiment No. 22. The appearance of the solution was clear, yellow, and unchanged.

23B (air atmosphere). Only a trace of precipitation appeared. The appearance of the solution had not changed.

23C (H₂S atmosphere). A yield of 1.195 grams of UO₂ was obtained, which gave a yield of available uranium of 44.24 per cent. This high yield compared favorably with the first experiments (No. 3). The solution at the end of the run was changed from a clear yellow to a cloudy green. However, upon exposure to air in filtering, the solution changed back to a clear yellow color. This green color indicated the presence of uranium sulfate (in a plus-4 valance, or reduced, state). If this is true the yield may have been limited by the amount of available oxygen.

These tests point up the fact that the reducing power of the constituents of the solution has a major effect on the precipitation of uraninite. Ferrous sulfate is a good reducing agent, but perhaps, in itself, not strong
enough. Hydrogen sulfide gas is a very powerful reducing agent, and its effect together with that of the ferrous ion may be ideal.

Experiment No. 24

The purpose of this experiment was to investigate the effect of the ferrous ion from different sources on the precipitation of uraninite from aqueous solution.

The solutions were prepared as follows:

24A--4.201 grams of uranyl sulfate and 0.2380 gram of iron filings (C.P. Fe) were placed in 20 grams of distilled water. \( \text{H}_2\text{S} \) was bubbled through the solution, and the tube was sealed. The uranium to iron ratio was 10 to 1.

24B--4.201 grams of uranyl sulfate and 2.380 grams of iron filings (C.P. Fe) were placed in 20 grams of distilled water. \( \text{H}_2\text{S} \) was bubbled through the solution, and the tube was sealed. The uranium to iron ratio was 1 to 1.

24C--1.187 grams of \( \text{FeSO}_4 \) (ferrous sulfate) were dissolved in 20 grams of distilled water. This solution was neutralized by the addition of two drops ammonium hydroxide. Hydrogen sulfide gas was bubbled through the solution. This gave a precipitate of black ferrous sulfide (FeS). To this suspension was then added 4.201 grams of uranyl sulfate which gave a uranium to iron ratio of 10 to 1. The tube was then sealed.

24D--4.201 grams of uranyl sulfate and 1.187 grams of ferrous sulfate were placed in 20 grams of distilled water. \( \text{H}_2\text{S} \) was bubbled through the solution. The tube was sealed. The uranium to iron ratio was 10 to 1. This tube was the "control."

Results--24A--As a result of the action of sulfuric acid on iron filings, hydrogen gas is generated. Since hydrogen gas is a very powerful reducing agent, the solution changed from the characteristic uranyl yellow to a bright green, even before the tube was sealed or any heat was applied. This green color is presumed to be from uranium sulfate formed by the
reduction of uranyl sulfate by the hydrogen gas. The yield of precipitate was 1.898 grams of UO₂ which represented a percentage yield of available uranium of 70.29 per cent.

24B-This tube burst during the digestion period. This was probably caused by internal pressure due to the liberation of hydrogen gas. The liquid and residue were removed from the interior of the autoclave and filtered. The residue contained a large amount of black material and the liquor was clear.

24C-This test gave the cleanest appearing precipitate of the four. The yield was 0.9720 gram of UO₂, or a percentage yield of available uranium of 36.00 per cent.

24D-In this test a large amount of ferric salts precipitated with the uraninite. The yield of UO₂ was 1.0691 grams which was a percentage yield of available uranium of 39.59 per cent.

The higher yield given by the iron filings was probably due to the increased amount of H₂ or H₂S. The difference was negligible when FeS or FeSO₄ was used.

Experiment No. 25

The purpose of this experiment was to check the feasibility of H₂S acting alone as the reducing agent.

The solutions were prepared as follows:

25A--4.201 grams of uranyl acetate were dissolved in 20 grams of distilled water. H₂S gas was bubbled through the solution, and the tube was sealed. No iron was present.

25B--1.187 grams of ferrous sulfate were dissolved in 20 grams of water. H₂S was bubbled through, and the solution was made basic with NH₄OH. The ferrous ions precipitated as FeS. 4.201 grams of uranyl sulfate were then added. More H₂S was bubbled through the solution, and the tube was sealed.

Both tests were placed in the autoclave for an accelerated digestion period of 48 hours.
Results—25A—A very clean black precipitate of UO$_2$ weighing 0.9743 gram, which was a yield of 36.08 per cent, was formed.

25B—A very clean black precipitate of UO$_2$ weighing 1.152 grams, which was a yield of 42.66 per cent, was formed.

These results show that the ferrous ion is not necessary for the reaction and that H$_2$S alone will precipitate uranium.

Experiment No. 26

The purpose of this test was to determine the feasibility of desulfurized natural gas acting as a precipitating agent on an aqueous solution of uranyl sulfate with no other reactant present.

The solutions were prepared as follows:

26A—4.201 grams of uranyl sulfate were dissolved in 20 grams of distilled water. Nothing else was added. Natural gas, desulfurized, was bubbled through the solution, and the tube was sealed.

26B—4.201 grams of uranyl sulfate was dissolved in 20 grams of distilled water. 1.187 grams of ferrous sulfate were added to the solution giving a uranium to iron ratio of 10 to 1. Natural gas, desulfurized, was passed through the solution, and the tube was sealed.

26C—4.201 grams of uranyl sulfate were dissolved in 20 grams of distilled water. Nothing else was added. Natural gas was bubbled through the solution. The H$_2$S content of the gas is not known. The tube was then sealed.

Results—26A gave only a trace of precipitation, far too low to be measured.

26B gave a light yield of approximately 1 to 2 per cent.

26C gave a very light yield, less than that of 26B, but larger than that of 26A.
These results indicate that the hydrogen sulfide content of natural gas is the constituent most conducive to precipitation. The ferrous ion, however, is a definite factor in the reduction. Natural gas with the hydrogen sulfide removed had very little effect on the reaction.

The results of the quantitative autoclave experiments are summarized in Table VII, Appendix.
STUDIES REGARDING THE ROLE OF WYOMING NATURAL GAS
IN PRECIPITATING PRIMARY URANIUM MINERALS
FROM PREGNANT SOLUTIONS

APPENDIX
The following elements were looked through and analyzed:

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.10</td>
</tr>
<tr>
<td>Ag</td>
<td>0.09</td>
</tr>
<tr>
<td>Re</td>
<td>0.001</td>
</tr>
<tr>
<td>Ge</td>
<td>0.0002</td>
</tr>
<tr>
<td>Co</td>
<td>0.0001</td>
</tr>
<tr>
<td>Pt</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

Note: The values are in parts per million (ppm).
Table II

Comparison of Typical Diffraction Pattern Analysis with Standard Pattern for UO$_2$

<table>
<thead>
<tr>
<th>Precipitate, Experiment No. 1</th>
<th>Measured Radius centimeters</th>
<th>Measured &quot;d&quot; Spacings, Angstrom units</th>
<th>U. S. Bureau of Standards Standard UO$_2$ &quot;d&quot; Spacings Angstrom units</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.490</td>
<td>3.127</td>
<td>3.157</td>
<td></td>
</tr>
<tr>
<td>2.860</td>
<td>2.731</td>
<td>2.735</td>
<td></td>
</tr>
<tr>
<td>4.105</td>
<td>1.930</td>
<td>1.934</td>
<td></td>
</tr>
<tr>
<td>4.870</td>
<td>1.646</td>
<td>1.649</td>
<td></td>
</tr>
<tr>
<td>5.110</td>
<td>1.575</td>
<td>1.579</td>
<td></td>
</tr>
<tr>
<td>6.000</td>
<td>1.364</td>
<td>1.368</td>
<td></td>
</tr>
<tr>
<td>6.620</td>
<td>1.253</td>
<td>1.255</td>
<td></td>
</tr>
<tr>
<td>7.625</td>
<td>1.153</td>
<td>1.163</td>
<td></td>
</tr>
<tr>
<td>8.215</td>
<td>1.0522</td>
<td>1.0523</td>
<td></td>
</tr>
<tr>
<td>9.210</td>
<td>0.9675</td>
<td>0.9666</td>
<td></td>
</tr>
<tr>
<td>9.845</td>
<td>0.9248</td>
<td>0.9243</td>
<td></td>
</tr>
<tr>
<td>10.055</td>
<td>0.9123</td>
<td>0.9114</td>
<td></td>
</tr>
<tr>
<td>10.985</td>
<td>0.8650</td>
<td>0.8646</td>
<td></td>
</tr>
<tr>
<td>11.765</td>
<td>0.8343</td>
<td>0.8339</td>
<td></td>
</tr>
<tr>
<td>12.045</td>
<td>0.8250</td>
<td>0.8243</td>
<td></td>
</tr>
<tr>
<td>13.480</td>
<td>0.7898</td>
<td>0.7903</td>
<td></td>
</tr>
</tbody>
</table>

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### Table III
Mineralogical Composition of Lucky Mac Ore

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount</th>
<th>Formula</th>
<th>Uranium %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uraninite</td>
<td>Major</td>
<td>$x\text{UO}_2 \cdot y\text{UO}_3$</td>
<td>88.2</td>
</tr>
<tr>
<td>Liebigite</td>
<td>Minor</td>
<td>$2\text{CaCO}_3 \cdot \text{U(CO}_3\text{)}_2 \cdot 10\text{H}_2\text{O}$</td>
<td>32.2</td>
</tr>
<tr>
<td>Sabugalite</td>
<td>Minor</td>
<td>$\text{HAI(UO}_2\text{)}_4 \cdot (\text{PO}_4\text{)}_4 \cdot 16\text{H}_2\text{O}$</td>
<td>53.6</td>
</tr>
<tr>
<td>Unknown &quot;H&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>Major</td>
<td>$\text{FeS}_2$</td>
<td></td>
</tr>
<tr>
<td>Unknown &quot;G&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selenium (Native)</td>
<td>Up to 2%</td>
<td>$\text{Se}$</td>
<td></td>
</tr>
<tr>
<td>Autunite</td>
<td>Major</td>
<td>$\text{Ca(UO}_2\text{)}_2 \cdot (\text{PO}_4\text{)}_2 \cdot 10-12\text{H}_2\text{O}$</td>
<td>45.4 to 48.2</td>
</tr>
<tr>
<td>Metaautunite</td>
<td>Major</td>
<td>$\text{Ca(UO}_2\text{)}_2 \cdot (\text{PO}_4\text{)}_2 \cdot 2.5 \text{ to 6.5 H}_2\text{O}$</td>
<td>45.4 to 48.2</td>
</tr>
<tr>
<td>Metatorbernite</td>
<td>Minor</td>
<td>$\text{Cu(UO}_2\text{)}_2 \cdot (\text{PO}_4\text{)}_2 \cdot 8\text{H}_2\text{O}$</td>
<td>50.8</td>
</tr>
<tr>
<td>Unknown &quot;T&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranophane</td>
<td>Minor</td>
<td>$\text{Ca(UO}_2\text{)}_2 \cdot \text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$</td>
<td>56.6</td>
</tr>
<tr>
<td>Rutherfordine</td>
<td>Minor</td>
<td>$\text{UO}_2\text{CO}_3$</td>
<td>72.1</td>
</tr>
<tr>
<td>Soddyite</td>
<td>Minor</td>
<td>$(\text{UO}_2\text{)}_5 \cdot (\text{SiO}_3\text{)}_2 \cdot (\text{OH})_6 \cdot 3\text{H}_2\text{O}$</td>
<td>71.6</td>
</tr>
<tr>
<td>Ilsmannite</td>
<td>Major</td>
<td>$\text{Mo}_3\text{O}_8 \cdot \text{nH}_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>Sulfur (Native)</td>
<td>Minor</td>
<td>$\text{S}$</td>
<td></td>
</tr>
<tr>
<td>Unknown &quot;N&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unknown &quot;F&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table IV

Summary of Results of Preliminary Experiment Nos. 1 through 5

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>U/Fe Ratio</th>
<th>Molality</th>
<th>Atmosphere</th>
<th>Retention Time Hours</th>
<th>pH Initial</th>
<th>pH Final</th>
<th>Temperature °C</th>
<th>Pressure psi</th>
<th>Presence of Uraninite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/1</td>
<td>0.5</td>
<td>H₂S</td>
<td>&gt;44/88</td>
<td>1.1</td>
<td>0.5</td>
<td>200</td>
<td>250</td>
<td>Strong</td>
</tr>
<tr>
<td>2</td>
<td>100/1</td>
<td>0.5</td>
<td>Natural Gas</td>
<td>&gt;44/88</td>
<td>1.0</td>
<td>0.7</td>
<td>200</td>
<td>250</td>
<td>Weak</td>
</tr>
<tr>
<td>3</td>
<td>100/1</td>
<td>0.5</td>
<td>H₂S</td>
<td>&gt;72/88</td>
<td>0.9</td>
<td>0.7</td>
<td>200</td>
<td>250</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>100/1</td>
<td>0.5</td>
<td>Desulfurized Natural Gas</td>
<td>&gt;72/88</td>
<td>0.9</td>
<td>0.8</td>
<td>200</td>
<td>250</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>100/1</td>
<td>0.5</td>
<td>Air</td>
<td>&gt;72/88</td>
<td>0.9</td>
<td>0.8</td>
<td>200</td>
<td>250</td>
<td>Trace</td>
</tr>
</tbody>
</table>
Table V
Summary of Results of Increased Temperature Experiment Nos. 6 through 13

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Distilled H₂O cc</th>
<th>GHW-20 cc</th>
<th>Salt A gm</th>
<th>GH-19 gm</th>
<th>Atmosphere</th>
<th>Time hrs</th>
<th>Temperature °C</th>
<th>Presence of Uraninite</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>30</td>
<td>6.302</td>
<td></td>
<td></td>
<td>H₂S</td>
<td>170</td>
<td>85</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>6.302</td>
<td></td>
<td></td>
<td>Air</td>
<td>170</td>
<td>85</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>6.302</td>
<td>1.0 dried</td>
<td>H₂S</td>
<td>170</td>
<td>85</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>6.302</td>
<td>1.0 free carbon</td>
<td>H₂S</td>
<td>170</td>
<td>85</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>6.302</td>
<td>1.0 native state</td>
<td>Air</td>
<td>170</td>
<td>85</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>6.302</td>
<td></td>
<td></td>
<td>Natural Gas</td>
<td>170</td>
<td>85</td>
<td>No</td>
</tr>
</tbody>
</table>

Uranyl Sulfate (UO₂SO₄) gm | Molality | U/Fe Ratio | Presence of Uraninite |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>3.151</td>
<td>0.25</td>
<td>- H₂S</td>
</tr>
<tr>
<td>13</td>
<td>3.151</td>
<td>0.25</td>
<td>Desulfurized Natural Gas</td>
</tr>
<tr>
<td>Experiment No.</td>
<td>UO$_2$SO$_4$ gms</td>
<td>Molality</td>
<td>U/Fe Ratio</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>14</td>
<td>6.302 (Salt C)</td>
<td>0.5</td>
<td>100/1</td>
</tr>
<tr>
<td>16</td>
<td>6.302 (Salt C)</td>
<td>0.5</td>
<td>100/1</td>
</tr>
<tr>
<td>17A</td>
<td>10 (Salt B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17B</td>
<td>10 (Salt B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17C</td>
<td>10 (Salt B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17D</td>
<td>10 (Salt B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18A</td>
<td>6.302 (Salt C)</td>
<td>0.5</td>
<td>100/1</td>
</tr>
<tr>
<td>18B</td>
<td>6.302 (Salt C)</td>
<td>0.5</td>
<td>100/1</td>
</tr>
<tr>
<td>18C</td>
<td>6.302 (Salt C)</td>
<td>0.5</td>
<td>100/1</td>
</tr>
<tr>
<td>19</td>
<td>10 (UO$_2$Cl$_2$) (FeCl$_2$)</td>
<td>-</td>
<td>100/1</td>
</tr>
</tbody>
</table>

1/ Salt B is leached Lucky Mac Ore.
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>( \text{UO}_2\text{SO}_4 \text{ gm} )</th>
<th>( \text{UO}_2\text{SO}_4 \text{ Molality} )</th>
<th>( \text{Ferrous Ion Source} \text{ gm} )</th>
<th>( \text{U/Fe Ratio} )</th>
<th>( \text{Atmosphere} )</th>
<th>( \text{Approximate Per Cent Available Uranium} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>22A</td>
<td>4.201</td>
<td>0.5</td>
<td>0.2373 FeSO(_4)</td>
<td>50/1</td>
<td>Helium</td>
<td>None</td>
</tr>
<tr>
<td>22B</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>Helium</td>
<td>Trace ?</td>
</tr>
<tr>
<td>22C</td>
<td>4.201</td>
<td>0.5</td>
<td>11.870 FeSO(_4)</td>
<td>1/1</td>
<td>Helium</td>
<td>1 - 2</td>
</tr>
<tr>
<td>23A</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>Helium</td>
<td>Trace</td>
</tr>
<tr>
<td>23B</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>Air</td>
<td>Trace</td>
</tr>
<tr>
<td>23C</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>44.24</td>
</tr>
<tr>
<td>24A</td>
<td>4.201</td>
<td>0.5</td>
<td>0.2380 Fe (Iron filings)</td>
<td>10/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>70.29</td>
</tr>
<tr>
<td>24B</td>
<td>4.201</td>
<td>0.5</td>
<td>2.380 Fe (Iron filings)</td>
<td>1/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>Tube Broke</td>
</tr>
<tr>
<td>24C</td>
<td>4.201</td>
<td>0.5</td>
<td>0.3751 FeS</td>
<td>10/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>36.00</td>
</tr>
<tr>
<td>24D</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>39.59</td>
</tr>
<tr>
<td>25A</td>
<td>4.201</td>
<td>0.5</td>
<td>None</td>
<td>-</td>
<td>( \text{H}_2\text{S} )</td>
<td>36.08</td>
</tr>
<tr>
<td>25B</td>
<td>4.201</td>
<td>0.5</td>
<td>0.3751 FeS</td>
<td>10/1</td>
<td>( \text{H}_2\text{S} )</td>
<td>42.66</td>
</tr>
<tr>
<td>26A</td>
<td>4.201</td>
<td>0.5</td>
<td>None</td>
<td>-</td>
<td>Desulfurized Gas</td>
<td>None</td>
</tr>
<tr>
<td>26B</td>
<td>4.201</td>
<td>0.5</td>
<td>1.187 FeSO(_4)</td>
<td>10/1</td>
<td>Desulfurized Gas</td>
<td>Light</td>
</tr>
<tr>
<td>26C</td>
<td>4.201</td>
<td>0.5</td>
<td>None</td>
<td>-</td>
<td>Natural Gas</td>
<td>Trace</td>
</tr>
</tbody>
</table>