CARBIDE AND CARBON CHEMICALS CORPORATION
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RESEARCH AND DEVELOPMENT DIVISION
Dr. B. D. Shipley, Director

CHEMICAL DEVELOPMENT DEPARTMENT
Mr. C. H. Clowett, Superintendent

PROGRESS REPORT ON CARBONITE STUDIES:
CARBONATE PROCESS
August, 1949

K. B. Brown
C. P. Coleman
W. R. Grimes

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Oak Ridge, Tennessee
September 8, 1949

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ORE SAMPLES

Recent shipments of ores to this laboratory for use in the Monticello studies have included samples labelled Radium 7, Stockpile 7, and Stockpile 9. Radium 7 is a normal, "salt-roast", ore. Stockpile 7 is a low vanadium, high lime ore such as will be processed by direct leaching, and Stockpile 9 is a low vanadium, low lime ore, also to be processed by direct leaching. The approximate chemical compositions of these ore samples are presented below in Table 1.

Table 1

Chemical Composition of Ores

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Radium 7</th>
<th>Stockpile 7</th>
<th>Stockpile 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₃O₈</td>
<td>0.46</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>2.9</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>86.3</td>
<td>77.0</td>
<td>82.7</td>
</tr>
<tr>
<td>CaO</td>
<td>3.3</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td>2.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.5</td>
<td>1.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.5</td>
<td>3.0</td>
<td>6.1</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.15</td>
<td>0.12</td>
<td>0.25</td>
</tr>
</tbody>
</table>

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THE CONTROL OF Na₂CO₃ IN PLANT LEACH LIQUORS

Usual practice for determining the Na₂CO₃ content of mill liquors has been to simply titrate the solutions, acidimetrically, to a methyl orange endpoint. However, due to the presence of varying amounts of vanadate salts, this method is not dependable.

In the laboratory, carbonate determinations are usually made by evolving CO₂, adsorbing the gas or some material such as ascarite, and weighing. Although this method can be highly accurate, it is, at the same time, too complex for routine use by a plant operator.

To gain sufficient accuracy, as well as simplicity of operation, a stepwise procedure may be presented as follows:

Procedure (Refer to Figure)

1. Pipette out a 5 ml sample of leach solution and place in one side of the divided Erlenmeyer flask (A).

2. Pipette 5 ml of 1M H₂SO₄ solution into the other side of flask A, taking care that the separation between the two liquids is clean.

3. Place Stopper B, fitted with a glass tube, in flask A.

4. Using the leveling bulb (D), adjust the water column in the burette to zero.

5. Connect the tygon tubing from the burette to the generator.
Figure 1 - Apparatus for Plant Determination of CO₂.
6. Make sure that all junctions are tight.
7. Lower the leveling bulb to a level which approximates the volume of gas to be measured.
8. Shake flask A, containing the sample, for one minute.
9. Wait five minutes, adjust the leveling bulb so that the water level in the bulb corresponds to the level in the burette, and read the volume.
10. The percentage carbonate can be read from a prepared graph.

Notes
a. To insure that no acid remains in the reaction flask from previous determinations, it should be good practice to rinse the flask thoroughly with water after each test, followed by a rinse in dilute caustic solution, followed by a final rinse with water.

b. The final connection of the reactor to the burette (step 8) is made at junction C rather than at stopper B so as to realize a minimum change in pressure in the system, which is sealed at this point.

Accuracy of Measurement
From a measurement of the volume of gas which is generated from any particular sample, the percentage carbonate may be calculated by applying the ideal gas laws. Using a standard sample size of 5 ml., we may calculate.
For example, let us assume that a 5 ml sample gave a gas volume of 81.3 ml; that the temperature is 30°C. (32 mm HgO vapor); and that the atmospheric pressure is 690 mm.

In this case,
\[ \% \text{MgCO}_3 = \frac{81.3 \times 273}{303 \times 580 - 32} \times \frac{106}{22400} \times \frac{100}{8} = 6 \]

The gas-volume method of analysis is affected mainly by temperature and pressure. Variation in volumes due to pressure, however, should be small. For simplicity, all calculations can be based on the average barometric pressure for the Monticello area. Extreme variations in atmospheric pressure should not be greater than ± 20 mm and thus the carbonate determination as calculated above should not suffer a relative error of greater than 1 - 3%.

Temperature variations must be given more serious consideration because (1) the fluctuations are greater and (2) the water vapor pressure is simultaneously affected. For instance, from a 5 ml sample of 5 percent carbonate solution at 30°C. and 580 mm, the volume of evolved gas would be as follows:

\[ \text{Volume} = \frac{\text{gas. MgCO}_3 \times \text{H. Temp. (abs.)} \times 760}{\text{atm. p} \times \text{HgO vapor p.} \times 106} \times 22400 \]
\[ = \frac{0.26 \times 303 \times 760}{275 \times 580 - 32} \times \frac{22400}{106} \]
\[ = 81.3 \text{ ml.} \]
At 59ºC, the results would be:

\[ \text{Volume} = 0.03 \times 324 \times 780 \times \frac{22.4 \text{L}}{100} \times 100 \]

In this case, a 5 percent change in measure volume would be obtained with temperature change of 10ºC.

Variations, caused by temperature, can be effectively reduced by furnishing the plant operator with charts showing the \( \text{Na}_{2}\text{CO}_3 \) (%) vs. gas-volume at different temperatures. A sample chart is presented in Figure 2. For these graphs, an average pressure at Mounicello of 580 cm has been assumed. If this pressure is not correct, new charts can be easily prepared.

Experimental Results

To test the procedure outlined above, a number of laboratory leach solutions were analyzed by the gas-volume method as well as by the standard evolution, direct weight method. Comparative answers by the two methods are presented below.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Gas Volume Method</th>
<th>Adsorption-Wt. Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock solution</td>
<td>2.7</td>
<td>2.9</td>
</tr>
<tr>
<td>Roast ore leach</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Raw ore leach</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Raw ore leach</td>
<td>5.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Raw ore leach</td>
<td>3.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Raw ore leach</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Stock solution</td>
<td>9.8</td>
<td>10.0</td>
</tr>
</tbody>
</table>
Figure 2. Gas Volume vs. Percent Na₂CO₃. Calculated on an Average Barometric Pressure of 560 mm of Hg for a Sample Volume of 5 ml.
On the basis of such data, it is believed that the gas-volatilization method is rapid and accurate.

CARBONATE CASCADE LEACHES ON RAW ORES

Data on the uranium and vanadium build-ups during cascade leaching of raw Indian Reservation ores were reported last month (Y-464). Results on the concentrations of other materials in the leach solutions are now available and these data are presented in Table 2.

Similar tests are being made with Stockpile 7 and Stockpile 9 ores, using 3 and 5 percent solutions of sodium carbonate. Since the maximum build-up of uranium has not yet been attained in any of these tests, the data will not be reported until next month. It may be mentioned that a treatment of Stockpile 7 ore with 3 percent Na₂CO₃ through seven stages has raised the uranium concentration to about 4 grams of U₃O₈ per liter. As the tests with Indian Reservation ore gave a maximum concentration of 4.8 grams of U₃O₈ per liter, it is probable that the Stockpile ores will also give results in this range.

Experiments with raw ores in general should be complete within the next month.
Table 2

Material Build-Up during Carbonate Cascade on
Raw Indian Reservation Ore - 2% Na₂CO₃

<table>
<thead>
<tr>
<th>Stage No.</th>
<th>gms. V₂O₅ per liter</th>
<th>gms. CO₂ per liter</th>
<th>gms. SiO₂ per liter</th>
<th>gms. PO₄³⁻ per liter</th>
<th>gms. Al per liter</th>
<th>% Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.9</td>
<td>3.6</td>
<td>0.08</td>
<td>0.11</td>
<td>0.03</td>
<td>2.64</td>
</tr>
<tr>
<td>2</td>
<td>4.7</td>
<td>7.1</td>
<td>0.09</td>
<td>0.20</td>
<td>0.08</td>
<td>2.65</td>
</tr>
<tr>
<td>3</td>
<td>4.7</td>
<td>10.0</td>
<td>0.15</td>
<td>0.13</td>
<td>0.25</td>
<td>2.99</td>
</tr>
<tr>
<td>4</td>
<td>4.8</td>
<td>13.4</td>
<td>0.08</td>
<td>0.10</td>
<td>0.09</td>
<td>2.87</td>
</tr>
</tbody>
</table>
CARBONATE CASCADE LEACHES ON SALT ROASTED ORE

For reasons explained in some detail in the previous month's report (Y-460), a repeat experiment on the 3 percent Na₂CO₃ cascade on salt roasted ore was conducted. The only differences in procedure between this and the former cascade were (1) the maintenance of a constant volume of leach liquor by attaching a reflux condenser to the leaching vessel, and (2) the practice of using only the pregnant liquor from one stage to the next without addition of either a carbonate or a water wash solution. These changes made it possible to avoid errors introduced when certain salts were redissolved during the washing operation.

The analytical data are not sufficiently complete to report in tabular form at the present time. However, it was found that the uranium concentration in the cascade solution increased regularly up to 3.8 grams of U₃O₈ per liter, and then decreased to about 1 gram of U₃O₈ per liter in subsequent stages. In short, the data indicate that a concentration of 3.8 grams of U₃O₈ per liter represents the maximum which can be obtained with a 3 percent Na₂CO₃ solution. The former cascade experiment indicated that a concentration of 3.6 grams of U₃O₈ per liter could be obtained before the greenish-yellow precipitate was observed to form during the leaching operation. The two cascade experiments appear to be in excellent agreement.

It has been shown above that the uranium concentration of cascade leachings on salt roasted ores suffers a marked drop upon continuing...
the cascade past the point of maximum build-up. Also, it has been mentioned that this change is accompanied by the precipitation of a greenish-yellow material from the leach liquors.

To gain some information as to the nature of this precipitate, some of the material was separated from the slurry, filtered, and redissolved for analyses. Since a thorough washing of the solid was not possible (it is fairly soluble in water), the determination was necessarily crude. It was possible to conclude from the data, however, that the precipitate is some complex compound of uranium and vanadium. Other studies of this material are being made, using refined techniques.

SOLUBILITY STUDIES ON SYNTHETIC AND NATURAL CARNOTITES

The studies on the solubility of synthetic carnotite (yellow-cake) and natural hand-picked carnotite in aqueous systems of sodium carbonate, sodium vanadate, and sodium chloride have been completed. These data have been reported in part in the progress reports for the past three months (Y-416, Y-441, and Y-460). For convenience, however, the previously reported data are included in this report along with the final data.

Effect of Sodium Carbonate Concentration

The influence of sodium carbonate concentration on the solubility of synthetic and natural carnotites is illustrated in Table 3 and

1 The values for sodium carbonate concentration were obtained by analyzing the solutions for total CO₂ evolved upon acidification and boiling, and converting to Na₂CO₃. Thus, any carbonate associated with the uranyl ion in the solution is included in the value for percent Na₂CO₃.
## Table 3

Effect of Sodium Carbonate Concentration on Solubility of Synthetic and Natural Carnotites (21°C)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Constituents Added</th>
<th>Na₂CO₃ in Sol'n (by analysis)</th>
<th>⁸⁷Sr Samples</th>
<th>⁸⁷Sr Samples</th>
<th>⁸⁷Sr Samples</th>
<th>Average Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>⁸⁷Sr U₂O₃ / gm.</td>
<td>⁸⁷Sr U₃PO₄ / liter</td>
<td>⁸⁷Sr U₃PO₄ / liter</td>
<td></td>
</tr>
<tr>
<td>V-767</td>
<td>1.0 gm. yellow cake</td>
<td>25 ml. of 3% sol'n</td>
<td>2.5</td>
<td>5.7</td>
<td>3.6</td>
<td>5.3</td>
</tr>
<tr>
<td>V-768</td>
<td>1.0 gm. yellow cake</td>
<td>25 ml. of 6% sol'n</td>
<td>5.5</td>
<td>9.2</td>
<td>5.5</td>
<td>10.0</td>
</tr>
<tr>
<td>V-769</td>
<td>1.0 gm. yellow cake</td>
<td>25 ml. of 12% sol'n</td>
<td>11.7</td>
<td>11.6</td>
<td>6.7</td>
<td>21.4</td>
</tr>
<tr>
<td>V-773</td>
<td>3.0 gm. carnitite</td>
<td>25 ml. of 3% sol'n</td>
<td>2.4</td>
<td>4.9</td>
<td>1.9</td>
<td>4.7</td>
</tr>
<tr>
<td>V-774</td>
<td>3.0 gm. carnitite</td>
<td>25 ml. of 6% sol'n</td>
<td>6.2</td>
<td>9.8</td>
<td>3.7</td>
<td>9.1</td>
</tr>
<tr>
<td>V-775</td>
<td>3.0 gm. carnitite</td>
<td>25 ml. of 12% sol'n</td>
<td>9.6</td>
<td>12.0</td>
<td>4.9</td>
<td>11.8</td>
</tr>
<tr>
<td>V-776</td>
<td>3.0 gm. carnitite</td>
<td>25 ml. of 12% sol'n</td>
<td>12.4</td>
<td>13.4</td>
<td>5.1</td>
<td>13.4</td>
</tr>
</tbody>
</table>

**Remarks:**

1. *A* samples were withdrawn 1 to 6 days after mixing the ingredients, *B* samples 2 to 3 weeks after mixing, and *D* samples from 8 to 10 weeks after mixing. *A* samples were taken 1 to 5 weeks after mixing, but analytical results were consistently low as shown by several check analyses, and the results, therefore, were discarded.

2. The *yellow-cake* contained 39.0% U and 10.8% V; the carnitite mineral contained 15.1% U and 3.66% V.

3. The average analyses were obtained by averaging the results of the *A*, *B*, and *D* samples.
Figure 3. It may be observed that from either of these uranium compounds the equilibrium uranium concentration in solutions of equal carbonate concentration is about the same. In a 3 percent Na₂CO₃ solution, the uranium concentration reaches 6 to 6 grams U₂O₅ per liter. Upon increasing the Na₂CO₃ concentration to 12 percent, the uranium concentration is increased in a near linear fashion to 13 to 14 grams U₂O₅ per liter.

It is evident that equilibrium conditions are approached rather rapidly in these determinations — the "A" samples, taken six days after mixing, are in excellent agreement with the "D" samples taken 70 days after mixing. The average analysis reported in Table 3 and used in constructing Figure 3 was obtained by averaging the results of the three separate samples.

Effect of Sodium Vanadate Concentration

The influence of sodium meta-vanadate concentration on the solubility of synthetic and natural cinnarites was determined by adding pure NaVO₃ to the system in varying amounts, while holding the Na₂CO₃ concentration constant. The data are contained in Table 4.

It appears that equilibrium conditions are attained much more slowly in systems containing added meta-vanadate. This is probably due to slow reactions in which the meta-vanadate ion converts to more complex species of polyvanadates. It is probable that equilibrium conditions were not reached in the data reported, although the "D" samples were taken 70 days after mixing.
Figure 3. Effect of Na<sub>2</sub>CO<sub>3</sub> Concentration on Solubility of Synthetic and Natural Carnotites
### Table 1

Effect of Sodium Vanadate Concentration on Solubility of Synthetic and Natural Carnottes (23°C.)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Constituents Added</th>
<th>Na₂CO₃ (gms.)</th>
<th>Na₃PO₃</th>
<th>% Na₂CO₃ in Sol'n (by analysis)</th>
<th>U²³⁵ Sample</th>
<th>U²³⁵ Sample</th>
<th>U²³⁵ Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-751</td>
<td>0.5 gm. yellow-cake</td>
<td>none</td>
<td>25 ml. of 3% sol'n</td>
<td>3.0</td>
<td>4.7</td>
<td>2.4</td>
<td>4.1</td>
</tr>
<tr>
<td>V-752</td>
<td>0.5 gm. yellow-cake</td>
<td>0.67</td>
<td>25 ml. of 3% sol'n</td>
<td>2.8</td>
<td>5.5</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>V-753</td>
<td>0.5 gm. yellow-cake</td>
<td>1.66</td>
<td>25 ml. of 3% sol'n</td>
<td>2.8</td>
<td>5.5</td>
<td>4.8</td>
<td>4.3</td>
</tr>
<tr>
<td>V-754</td>
<td>0.5 gm. yellow-cake</td>
<td>2.68</td>
<td>25 ml. of 3% sol'n</td>
<td>2.8</td>
<td>5.5</td>
<td>4.8</td>
<td>4.0</td>
</tr>
<tr>
<td>V-755</td>
<td>3.0 gm. carnottite</td>
<td>none</td>
<td>25 ml. of 3% sol'n</td>
<td>2.4</td>
<td>4.9</td>
<td>2.9</td>
<td>4.8</td>
</tr>
<tr>
<td>V-756</td>
<td>3.0 gm. carnottite</td>
<td>0.67</td>
<td>25 ml. of 3% sol'n</td>
<td>2.6</td>
<td>4.9</td>
<td>2.9</td>
<td>4.6</td>
</tr>
<tr>
<td>V-757</td>
<td>3.0 gm. carnottite</td>
<td>1.17</td>
<td>25 ml. of 3% sol'n</td>
<td>2.3</td>
<td>3.8</td>
<td>3.8</td>
<td>3.2</td>
</tr>
<tr>
<td>V-758</td>
<td>3.0 gm. carnottite</td>
<td>1.66</td>
<td>25 ml. of 3% sol'n</td>
<td>2.3</td>
<td>3.8</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>V-759</td>
<td>3.0 gm. carnottite</td>
<td>3.25</td>
<td>25 ml. of 3% sol'n</td>
<td>2.2</td>
<td>2.9</td>
<td>2.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The remarks made under Table 3 may also be used in these data.
The sodium vanadate concentration served to exert only a slight effect on the solubility of synthetic carnitite, even in concentrations as high as 70 gm. V₂O₅ per liter. A considerably greater effect was exhibited on the natural carnitite mineral; the uranium concentration decreased quite regularly from a value of 5 grams U₃O₈/liter to a value of 2 grams U₃O₈/liter, when the vanadium concentration was increased from 3.0 to 70 gm. V₂O₅/liter. The difference in behavior of synthetic and natural carnitites is not understood at the present time.

**Effect of Sodium Chloride Concentration**

The influence of sodium chloride concentration on the solubility of synthetic and natural carnitites was determined by adding NaCl to the system in varying amounts, while holding the Na₂CO₃ concentration constant. These data were reported in full in the July Progress Report, Y-460, and will not be included in this report.

It was found that the amount of uranium dissolved from both synthetic and natural carnitites is practically independent of sodium chloride concentration, at least up to concentrations of about 12 percent.

**Effect of Sodium Vanadate in Combination with Sodium Chloride**

The influence of sodium vanadate in the absence of sodium chloride, and sodium chloride in the absence of sodium vanadate was determined as previously discussed. It was then felt that one series of runs should be made in which both these salts were present in varying amounts. These data were obtained only on natural carnitite (Table 6).
Table 5

Effect of Sodium Vanadate in Combination with Sodium Chloride on the Solubility of Natural Carronite

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Constituents Added</th>
<th>Na₂CO₃ (%)</th>
<th>Na₂CO₃ (gm.)</th>
<th>NaCl (by analysis)</th>
<th>% NaCl</th>
<th>&quot;A&quot; Samples</th>
<th>% NaCl</th>
<th>&quot;B&quot; Samples</th>
<th>% NaCl</th>
<th>&quot;C&quot; Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>Na₂CO₃</td>
<td>NaCl</td>
<td>% NaCl</td>
<td>gms. V₂O₅/g</td>
<td>gms. V₂O₅/g</td>
<td>gms. V₂O₅/g</td>
<td>gms. V₂O₅/g</td>
<td>gms. V₂O₅/g</td>
<td></td>
</tr>
<tr>
<td>V-751</td>
<td>25 ml. of 3% sol'n</td>
<td>none</td>
<td>none</td>
<td>2.6</td>
<td>0.0</td>
<td>5.0</td>
<td>2.1</td>
<td>5.3</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>V-752</td>
<td>25 ml. of 3% sol'n</td>
<td>0.67</td>
<td>1.00</td>
<td>2.2</td>
<td>2.8</td>
<td>4.2</td>
<td>17.5</td>
<td>4.1</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>V-753</td>
<td>25 ml. of 3% sol'n</td>
<td>0.67</td>
<td>1.00</td>
<td>3.3</td>
<td>3.6</td>
<td>8.4</td>
<td>39.2</td>
<td>9.4</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>V-754</td>
<td>25 ml. of 3% sol'n</td>
<td>0.67</td>
<td>1.00</td>
<td>10.8</td>
<td>3.7</td>
<td>11.1</td>
<td>20.4</td>
<td>12.4</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>V-755</td>
<td>25 ml. of 3% sol'n</td>
<td>1.24</td>
<td>2.00</td>
<td>2.4</td>
<td>7.4</td>
<td>4.2</td>
<td>33.9</td>
<td>4.4</td>
<td>32.7</td>
<td></td>
</tr>
<tr>
<td>V-756</td>
<td>25 ml. of 3% sol'n</td>
<td>1.92</td>
<td>3.00</td>
<td>3.0</td>
<td>11.0</td>
<td>1.1</td>
<td>20.6</td>
<td>1.2</td>
<td>29.3</td>
<td></td>
</tr>
</tbody>
</table>

Remarks:

1. 1.0 gms. of carnalite mineral added in each case (39.6% U, 10.8% V).
2. "A" samples were withdrawn 5 days after mixing the ingredients, "B" samples 15 days after mixing, and "C" samples 36 days after mixing.
3. Note in Experiments V-754 and 756 that the high NaCl concentration appears to limit the solubility of Na₂CO₃. Had all the Na₂CO₃ gone into solution, the vanadium concentration should be about 50 and 60 gms. U₅O₈/liter, respectively.
It may be observed in experiments V-792, -3, -4, in which the concentrations of NaCl and NaVO₃ were held constant, and the Na₂CO₃ concentration varied from 3 to 10 percent, that the uranium concentration increased with carbonate concentration in much the same manner as was obtained in the absence of NaCl and NaVO₃, but to a lesser degree.

In experiments V-792, -5, -6, the weight ratio of NaCl to NaVO₃ added to each was held constant, but the amount was increased regularly, and the Na₂CO₃ concentration was held constant at about 3 percent. It may be noted that the uranium concentration is decreased with the increase in vanadate concentration in about the same manner as was obtained in the absence of NaCl (see Table 4). However, the uranium concentration does not decrease regularly with time as was the case with the high vanadium runs in the absence of sodium chloride. The equilibrium conditions appear to be reached more rapidly when sodium chloride is present.

Solubility of Carnotite Mineral in Actual Leach Liquors

All systems discussed thus far were prepared by mixing the carnitite mineral with sodium carbonate solutions to which pure sodium metavanadate and pure sodium chloride were added as desired. It was felt that some data should be obtained by using solutions derived from actual leaching of salt roasted ores. Therefore, a series of experiments were treated with an excess of carnitite mineral (Table 6).

It may be observed in experiment V-301 that a typical leach liquor
Table 6
Solubility of Carnotite Mineral in Actual Leach Liquors

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Source</th>
<th>Leach Liquor Used</th>
<th>% Na₂CO₃ in Final Solution</th>
<th>% NaCl in Final Solution</th>
<th>&quot;A&quot; Samples</th>
<th>&quot;B&quot; Samples</th>
<th>&quot;C&quot; Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% Na₂CO₃/ liter</td>
<td>% Na₂CO₃/ liter</td>
<td>% Na₂CO₃/ liter</td>
</tr>
<tr>
<td>V-501</td>
<td>25 ml. of stock sol'n</td>
<td>2.3</td>
<td>28</td>
<td>2.7</td>
<td>3.1</td>
<td>9.2</td>
<td>4.6</td>
</tr>
<tr>
<td>V-502</td>
<td>25 ml. of stock sol'n</td>
<td>2.3</td>
<td>28</td>
<td>2.7</td>
<td>5.6</td>
<td>9.6</td>
<td>8.9</td>
</tr>
<tr>
<td>V-603</td>
<td>25 ml. cascade exp. L-591</td>
<td>3.3</td>
<td>36</td>
<td>5.2</td>
<td>6.0</td>
<td>10.9</td>
<td>8.8</td>
</tr>
<tr>
<td>V-604</td>
<td>25 ml. cascade exp. L-532</td>
<td>4.2</td>
<td>45</td>
<td>5.0</td>
<td>5.7</td>
<td>12.5</td>
<td>9.3</td>
</tr>
<tr>
<td>V-605</td>
<td>25 ml. cascade exp. L-551</td>
<td>3.6</td>
<td>36</td>
<td>8.5</td>
<td>8.0</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>V-606</td>
<td>25 ml. cascade exp. L-501</td>
<td>4.5</td>
<td>45</td>
<td>8.5</td>
<td>7.5</td>
<td>12.3</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Remarks:
1. 3.0 gm. carnotite mineral added in each case (39.0% U, 10.8% V).
2. In experiments V-501 and V-502, the stock solution was fortified with dry Na₂CO₃ to boost the Na₂CO₃ concentration to about 3 and 6%, respectively.
3. "A" samples were withdrawn 4 days after mixing the ingredients, "B" samples 14 days after mixing, and "C" samples 35 days after mixing.
containing 2.5 grams UO$_2$O$_2$/liter and 28 grams V$_2$O$_5$/liter is capable of
dissolving additional uranium up to a concentration of 4.6 grams
UO$_2$O$_2$/liter in a 6 percent sodium carbonate solution. Upon adjusting
the sodium carbonate concentration of this typical leach liquor to
about 6 percent Na$_2$CO$_3$ (experiment V-802), the uranium concentration
was increased to 9 grams UO$_2$/liter.

In other experiments (V-805.1, -4, -5, -6) in which leach liquors
containing from 3.5 to 4.5 grams UO$_2$O$_2$/liter were used, the uranium
concentration was increased in a similar manner, the value in each case
being primarily dependent on the sodium carbonate concentration.

SOLUBILITY STUDIES ON SODIUM URANYL CARBONATE

In the previous month's report (Y-480), the preparation of this
salt was described, and some data were presented on its solubility in
aqueous systems containing varying amounts of sodium salts of carbonate,
chloride, and metavanadate. The data on the previously reported
experiments are completed in the present report, and additional infor­
mation is presented on the effect of sodium chloride concentration on
the solubility of sodium uranyl carbonate (Table 7).

Effect of Sodium Carbonate Concentration

The influence of sodium carbonate concentration on the solubility
of sodium uranyl carbonate is illustrated by experiments V-781, 2, and
3. It is apparent that the solubility of this salt decreases markedly
with sodium carbonate concentration. About 70 gm. UO$_2$/liter may be
The procedure is explained in detail in Table 5 of the July Progress Report, X-660.

For V-761 Series - "A" samples were withdrawn 2 days after mixing, "B" samples 20 days, and "C" samples 50 days after mixing.

For V-811 Series - "A" samples were withdrawn 8 days after mixing, and the "B" samples 30 days after mixing.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Solvent (25 ml. volumes)</th>
<th>Sodium Uanyl Carbonate (mg.)</th>
<th>NaNO₃ (mg.)</th>
<th>NaCl (mg.)</th>
<th>% Na₂CO₃ (by analysis)</th>
<th>% NaCl (by analysis)</th>
<th>Uranium (ppm, U₂O₅/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-761</td>
<td>Water</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>31.3</td>
</tr>
<tr>
<td>V-762</td>
<td>25% Na₂CO₃</td>
<td>3.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>63.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>42.1</td>
</tr>
<tr>
<td>V-763</td>
<td>65% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>49.4</td>
</tr>
<tr>
<td>V-764</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>32.1</td>
</tr>
<tr>
<td>V-765</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>31.3</td>
</tr>
<tr>
<td>V-766</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>2.00</td>
<td>2.00</td>
<td>5.3</td>
<td>7.9</td>
<td>31.3</td>
</tr>
<tr>
<td>V-811</td>
<td>Water</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>39.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>26.5</td>
</tr>
<tr>
<td>V-812</td>
<td>25% Na₂CO₃</td>
<td>3.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>6.1</td>
</tr>
<tr>
<td>V-813</td>
<td>65% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
</tr>
<tr>
<td>V-814</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
</tr>
<tr>
<td>V-815</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
</tr>
<tr>
<td>V-816</td>
<td>35% Na₂CO₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Note: The table shows the results of solubility studies on sodium uanyl carbonate with different solvents and conditions.
obtained in a water solution; this is reduced to about 50 g. UO₂Cl₂/liter in a 3 percent \( \text{Na}_2\text{CO}_3 \) solution, and further reduced to about 30 g. \( \text{UO}_2\text{Cl}_2 \)/liter in a 5 percent \( \text{Na}_2\text{CO}_3 \) solution. It is of interest to mention that the data are in good agreement with that obtained by investigators at Princeton University.¹

**Effect of Sodium Vanadate Concentration**

It may be observed from experiments V-794 and 795 that sodium metavanadate in concentrations of 10 to 20 g. \( \text{V}_2\text{O}_5 \)/liter tends to decrease the solubility in 3 percent \( \text{Na}_2\text{CO}_3 \) solution from about 50 g. \( \text{UO}_2\text{Cl}_2 \)/liter to about 35 g. \( \text{UO}_2\text{Cl}_2 \)/liter. Further data on the effect of sodium vanadate were not obtained, since it appeared that its effect was much less than that of sodium chloride.

**Effect of Sodium Chloride Concentration**

The very pronounced effect of sodium chloride concentration on the solubility of sodium uranyl carbonate as shown by the preliminary experiment V-786 prompted further study of this phenomenon. A series of experiments was conducted in which the \( \text{NaCl} \) concentration in 3 percent \( \text{Na}_2\text{CO}_3 \) solution was varied from 2 percent to 15 percent. As shown by experiments V-812 through V-816, the solubility of sodium uranyl carbonate decreases regularly with \( \text{NaCl} \) concentration. In Figure 4 this effect is illustrated by plotting the uranium concentration against

¹ Purcell, Kundt, and Bruce, "The Solubility of Sodium Uranyl Carbonate in Water and in Solutions of Various Salts".

FOR OFFICIAL USE ONLY
Figure 4. Effect of NaCl and NaVO₃ Concentration on Solubility of Sodium Urenyl Carbonate in 5% Na₂CO₃ Solution.
the molarity of the solution in NaCl. Included in this plot are the
two experiments on NaWO₄ effect (V-784-6). Since the NaWO₄ data
appear to fall on the curve for NaCl effect, it may be speculated that
the vanadate ion has no particular effect on the solubility of sodium
uranyl carbonate in the range of vanadate concentration studied. It
would appear that the sodium ion, the only ion common to the salt
being studied, exerts the most important effect.

Future Work:
The differences observed in the data from studies of the solu-
bilities of yellow cake, carnocite, and sodium uranyl tricarbonate
under similar conditions are quite interesting. It is possible that
some fundamental studies will be made of this system as a part of
another program at Y-12.

CARBONATE CONSUMPTION DURING LEACHING

The consumption of carbonate during direct leaching treatments of
raw ores should be quite low. Potential consumers (such as compounds
of calcium and magnesium) are, at least for the main part, already
present in the carbonate form. In addition, since only minor quantities
of materials are dissolved by the carbonate solution, losses due to the
following type of reaction should also be small.

\[ V_2O_5 + Na_2CO_3 = 2 NaWO_3 + CO_2 \]

Rough experimentation with Stockpiles 7 and 9 ores has indicated
that the Na₂CO₃ consumption by direct leaching is in the order of 1 gram
per 100 grams of ore. Since each ton of ore in the plant will be con-
tacted with 3 tons of 5 percent Na₂CO₃ solution, it is probably safe to
assume that the carbonate concentration in thickener No. 1 will not
change more than a few tenths of one percent.

In the case of salt-roast ores, in which the CaCO₃ has been decom-
posed by heating, a larger consumption of carbonate may be incurred.
More accurate determinations of carbonate consumption are being made
for both raw and roasted ores.

MISCELLANEOUS

1. To prepare a quantity of typical leach liquors for precipitation
studies, large scale leachings have been conducted in which Stockpile
ore was treated, in cascade fashion, with 5 percent solutions of Na₂CO₃.
Ten gallons of typical leach liquors have been prepared — ranging from
1 to 2 grams per liter in U₃O₈.

2. It has been mentioned previously that the carbonate leach solutions
from direct treatments of raw ores are strongly discolored by a blackish-
brown material. Since it was found that this substance could be coagu-
lated by making the solution strongly acidic, a few simple tests were
made to determine whether the material is inorganic or organic in nature.

Upon ignition, essentially all of the solid was combustible. The
material is obviously organic — probably humus.
II. THE RECOVERY OF URANIUM AND VANADIUM FROM CARBONATE LIQUORS

Dr. C. F. Coleman in charge
Miss E. J. Lord and
Mr. F. G. Seeley assisting

INTRODUCTION

Yellow-cake precipitations from raw leach liquors have shown at best five ppm uranium in the filtrates. There is some evidence that this amount of uranium is unavailable because it is held by a dark material, apparently organic, which seems to be characteristic of these leach liquors. However, most of these tests were made with small volumes, and lower filtrates may be obtained when larger quantities of these liquors are available. Ten ppm uranium in the filtrate probably will be considered satisfactory operation, so that improvement will contribute mainly to a convenient operating margin.

In the red-cake precipitation study, the effects of over-all concentration and of sodium ion concentration have been examined more thoroughly, and the effect of phosphate has been tested. At high concentrations of sodium ion, either as chloride or sulfate, the rate of precipitation was greatly increased. A small amount of phosphate retarded the precipitation markedly. Analyses have not been reported to show whether the phosphate contaminated the vanadium product.
YELLOW-OXIDE PRECIPITATION

Yellow-oxide precipitations from carbonate leaches of raw ores have been less nearly complete than has been usual with synthetic solutions or leaches of salt-roasted ores. A liquor from raw Indian Reservation ore was an exception, giving a filtrate below two ppm uranium (Table 1, p. 10, T-460). Other raw leach liquors have given filtrates at around ten ppm uranium.

With the exception of the liquor from the Indian Reservation ore, the raw leach liquors have all contained an opaque, dark brown substance, apparently organic, in solution or stable dispersion. It is possible that uranium amounting to 5 or 10 ppm is chemically or physically bound to this material. This is supported by the results of Run No. L-64 (Table 1): After the dark material was removed by treatment with Norrit "A" activated charcoal, yellow-oxide precipitation proceeded in the usual manner to a filtrate of 0.4 ppm uranium.

Aside from the higher filtrates obtained, the raw leach liquors have shown a little more tendency for drift of pH, and a tendency to foam which may be troublesome in the precipitation tanks. The cakes were dark, and contained less vanadium than has been usual.
## Table 1

### Yellow-Cake Precipitation

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L-55</td>
<td>I</td>
<td>1</td>
<td>21.6</td>
<td>5.5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>L-56</td>
<td>III</td>
<td>0.15</td>
<td>2.6</td>
<td>7.0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>L-58</td>
<td>IV</td>
<td>0.15</td>
<td>1.7</td>
<td>4.9</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>L-59</td>
<td>IV</td>
<td>0.15</td>
<td>1.7</td>
<td>7.0</td>
<td>6</td>
<td>130</td>
</tr>
<tr>
<td>L-60</td>
<td>IV</td>
<td>0.15</td>
<td>1.6</td>
<td>7.2</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>L-61</td>
<td>N-1</td>
<td>14</td>
<td>7.4</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-62</td>
<td>IV</td>
<td>0.15</td>
<td>6.7</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-63</td>
<td>IV</td>
<td>0.15</td>
<td>6.5</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-64</td>
<td>IV a.</td>
<td></td>
<td></td>
<td></td>
<td>(long digestion: 7.8</td>
<td>10)</td>
</tr>
<tr>
<td>L-65</td>
<td>IV a.</td>
<td>0.15</td>
<td>7.5</td>
<td>0.4</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>

### Solutions:

1. Carbonate leach after low-temperature bake of Cactus Nat ore: 4.6% Na₂CO₃, 0.06% Cl, 0.06% U, 0.03% V.

2. Carbonate leach of raw ore, Stock-File No. 7: About 5% Na₂CO₃, 0.22% U, 0.06% V.

3. Carbonate leach of raw ore, Stock-File No. 9: About 5% Na₂CO₃, 0.18% U, 0.06% V.

4. Solution IV treated with activated charcoal to remove most of the colored material.

5. A normal pregnant liquor from the Naturita Plant of V.C.A.
Table 2

Composition of Yellow Cake

<table>
<thead>
<tr>
<th>No.</th>
<th>Water</th>
<th>V, %</th>
<th>V, %</th>
<th>Molar Ratio, U/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-56</td>
<td>72</td>
<td>40</td>
<td>6.9</td>
<td>0.96</td>
</tr>
<tr>
<td>L-59</td>
<td>75</td>
<td>40</td>
<td>6.7</td>
<td>1.28</td>
</tr>
<tr>
<td>L-63</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>L-64</td>
<td>72</td>
<td>-</td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>
RED CAKE PRECIPITATION

The effects of dilution of varying salt concentration and of phosphate on the rate of precipitation are shown in Figures 5 to 8. (The coordinates for these curves are on the same scale as for the curves previously reported.)

The dilution tests differed from those previously reported in that solutions for the earlier set were diluted with waste liquor, so that the salt concentrations remained about constant, whereas the solutions in the present series were diluted with water. This series also contains two solutions (S-36 and -38, Figure 5) which were evaporated to higher concentrations than the natural head solution.

Comparison of the present with the former results (Figure 1, p. 81, Y-44) shows that both vanadium concentration and total salt concentration affect the rate of precipitation.

Figures 6 and 7 show the effects of varying the sodium chloride and the sodium sulfate concentrations; a large increase of either salt markedly hastened the precipitation.

The effect of phosphate is shown in Figure 8. The maximum amount of phosphate added in this series (1.42 g, PO₄/K, S-47) was 0.2 mole PO₄ per mole V. The cakes were washed and submitted for phosphate analysis, which has not been reported.
FIGURE 5
RATE OF RED-CAGE PRECIPITATION
EFFECT OF DILUTION
Head Solution: Purified Liquor from Leach Solution
S-1 (Naturite)
(S-34: Initial concentration, 32.4 g V2O5/L)
(S-35: Initial concentration, 25.8 g V2O5/L)
FIGURE 6
RATE OF RED-CABE PRECIPITATION
EFFECT OF SODIUM CHLORIDE CONCENTRATION
Head Solution: Purified Liquor from Leach Solution S-1 (Mature)
NaCl: S-37, 12.7 g/l
S-40, 21.2 g/l
S-41, 43.5 g/l
S-42, 72.7 g/l
FIGURE 7

RATE OF RED-CANE PRECIPITATION

EFFECT OF SODIUM SULFATE CONCENTRATION

Head Solution: Purified Liquor from Leach Solution
M-1 (Maturita)

\[
\begin{align*}
\text{MgSO}_4 &: \begin{array}{c}
S-37, 65 \text{ g/L} \\
S-43, 75 \text{ g/L} \\
S-44, 109 \text{ g/L} \\
S-45, 139 \text{ g/L} \\
S-46, 204 \text{ g/L}
\end{array}
\end{align*}
\]

Grain Yr % / Liter

Time (hours)
FIGURE 6
RATE OF RED-CAKE PRECIPITATION
EFFECT OF PHOSPHATE

Head Solution: Purified Liquor from Leach Solution
S-1 (Borax)

PO₄: S-37, 0
S-49, 0.35
S-49, 0.71
S-47, 1.48

Gross %PO₄ / hour

Time (hours)
IRON VANADATE PRECIPITATION

Study has been started of precipitation of ferrous and ferric vanadates from carbonate liquors after yellow-cake precipitation. Initial results indicate that the precipitation will be satisfactory for recovery of vanadium in low-level effluents (e.g., 0.2 to 2 g. \(V_2O_5/1\)).

FLUORESCENT BEAD TEST FOR URANIUM

The critical level is expected to be about 10 ppm uranium in the filtrate, and a precision range of \(x^{1/2}\) to \(x^2\) is expected to be satisfactory for the test.

Bead-loops were made of No. 20 platinum wire, loops 3.5 to 4 mm I.D., welded for rigidity. A flat bead of sodium fluoride formed in the loop weighs about 30 mg.

Drop-loops were made by flattening the round loops to an inside width of 1.3 to 1.5 mm. These loops transfer about 3 microliters.

A comparison scale was made by sealing into a lucite strip a blank bead and ten beads with graduated amounts of uranium. The quantities of uranium added were in geometric progression \((x2)\) from 1 millimicrogram to 0.5 microgram; however, the scale is not to be used as an absolute standard, but the cut-off point is to be determined by testing a standardized solution.
For a critical level of the order of 10 ppm, the bead size and drop size obtained permit direct testing without dilution of the filtrate. The sensitivity (ability to distinguish between successive beads) is much lower than in tests with large fluorescent discs, but appears to be sufficient for the purpose.
III. ANALYTICAL DEVELOPMENT

Mr. W. H. Grimes in charge
Messrs. J. D. Redman, O. J. Nessle
and Miss Nancy Boane assisting

1. Titration for uranium in most head samples, stored pregnant
   liquors, yellow-cake, and UO₂ product.

2. Colorimetric determination (ascorbic acid) for some head
   samples, calcines, carbonate-soluble uranium in calcines, and pregnant
   liquors.

3. Fluorimetric determination for carbonate-insoluble uranium
   in calcines, tailings, carbonate-soluble uranium in tailings, yellow-cake
   filtrate, and red-cake filtrate.