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SOME DESIGN ASPECTS OF THE PRESSURE-OXIDATION ACID LEACHING OF A CANADIAN URANIUM ORE

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Technical Bulletin TB 110

Price 75 cents

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Catalogue No. M34-20/110

Price subject to change without notice

Queen's Printer for Canada Ottawa, 1970

Mines Branch Technical Bulletin TB 110

SOME DESIGN ASPECTS OF THE PRESSURE-OXIDATION ACID LEACHING OF A CANADIAN URANIUM ORE

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J.A. Vezina* and W.A. Gow**

ABSTRACT

An investigation was done to determine the amount of heat and compressed air or oxygen required to leach Elliot Lake ore by pressure-oxidation, acid leaching. The tests were done on a batch scale with the leaching being done in a 50-gallon autoclave. The results showed that 95% of the uranium was extracted from a typical Elliot Lake ore in three hours at a temperature of 302°F, a total gas pressure in the autoclave of 150 psi gauge and an oxygen partial pressure of about 9 psi absolute. To maintain these conditions when the oxygen is supplied as compressed air would require 2207 cubic feet of dry air and 310,929 BTU per ton of ore.

Conditions to obtain up to 96% uranium extraction in as little as two hours were also determined. The highest extraction rates and extractions, which were obtained with oxygen partial pressures of about 20 psi absolute, would necessitate the oxygen being supplied as compressed oxygen.

The cost of heat and compressed air or oxygen to extract 95-96 per cent uranium in 2 to 4 hours by acid pressure oxidation would be in the range of 0.39 to 0.57 per ton of ore treated.

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INTRODUCTION

The extraction of uranium from ores containing iron sulphide minerals by pressure oxidation has been reported by various authors (1,2,3). It has been proposed that oxygen under pressure oxidizes the iron sulphide minerals to produce sulphuric acid and ferric compounds, and oxidizes tetravalent uranium to the acid-soluble hexavalent form. It has been suggested that the pressure oxidation of a uranium ore containing pyrite proceeds according to the following equations: (2).

- $2 \operatorname{FeS}_{2} + 70_{2} + 2 \operatorname{H}_{2}O \longrightarrow 2 \operatorname{FeSO}_{4} + 2\operatorname{H}_{2} \operatorname{SO}_{4}, \qquad (Eq 1)$
- $2 \operatorname{FeSO}_{4} + \operatorname{H}_{2}\operatorname{SO}_{4} + \frac{1}{2} \operatorname{O}_{2} \longrightarrow \operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + \operatorname{H}_{2}\operatorname{O}, \qquad (\operatorname{Eq} 2)$
- $\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + 6 \operatorname{H}_{2}O \longrightarrow 2 \operatorname{Fe}(\operatorname{OH})_{3} + 3 \operatorname{H}_{2}\operatorname{SO}_{4}$ (Eq 3)
- $\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + (2+2x)\operatorname{H}_{2}O \longrightarrow 2 \operatorname{Fe}(\operatorname{OH})\operatorname{SO}_{4}.x\operatorname{H}_{2}O + \operatorname{H}_{2}\operatorname{SO}_{4}, \quad (\operatorname{Eq} 4)$

The rate of dissolution of uranium from ores during pressure oxidation with oxygen has been shown to depend mainly on five These are temperature, oxygen partial pressure, ore size, factors. pulp density, and the degree of agitation to which the pulp is subjected. From the previously published work on pressure leaching, it is indicated that the extraction of 95 per cent of the uranium could be obtained from an Elliot Lake uranium ore if it were ground to 85 per cent minus 200 mesh, slurried to 60 per cent solids by weight and leached for four hours with vigorous agitation under air or pure oxygen to give an oxygen pressure of 15 psia at a temperature of 302°F. This rate of extraction is considerably faster than the 50 to 70 hours usually required to dissolve the same amount of uranium from Elliot Lake ore by conventional acidleaching practice currently used in that area.

Previously published work has also demonstrated that the extraction of uranium by pressure leaching was technically feasible. However, the published literature is sketchy on the information needed to determine the economics of the process. In essence, pressure oxidation differs from the normal sulphuric acid leaching atmospheric process in that the process uses compressed air or oxygen, a higher temperature and more vigorous agitation of the pulp. The work reported in this paper was done to determine the cost of the heat and compressed air, needed to leach an Elliot Lake ore by the pressure-oxidation process in a period of three to four hours. The amount of compressed air required to provide the oxygen used in the leaching was determined from large-scale leaching tests done in about 30-gallon batches. As the oxygen is used up by the reaction of Equations 1 and 2, the air in the autoclave becomes depleted in oxygen. The partial pressure of oxygen is maintained at the desired level by bleeding the oxygen-depleted air from the autoclave and feeding fresh compressed air to the autoclave at suitable rates.

All the tests in this study were done, at a temperature of 302° F., on ore ground to about 85 per cent minus 200 mesh, and a pulp density of 60 per cent solids. The effects of increasing the total pressure from 100 to 150 psig, and of increasing the oxygen partial pressure from 2 to 19 psia were investigated. Oxygen partial pressures greater than 11 psia were maintained by adding oxygen to the test in the form of pure oxygen rather than air.

PROCEDURE

The tests were carried out with uranium ore supplied through the courtesy of Denison Mines Limited, Elliot Lake, Ontario. Chemical analyses of the ore used as feed in this study are shown in Table 1.

The tests were carried out in a glass-lined, steam-jacketed 50-gallon autoclave. The compressed air and oxygen were introduced into the pulp through a half-inch-ID stainless steel pipe. Vigorous agitation of the pulp was provided by a three-bladed, glasscoated agitator, propelled by an electric motor through a reductiongear mechanism; the actual rotational speed of the agitator was 450 rpm. The pulp was sampled every hour by closing the compressed air inlet and depressurizing the compressed-air inlet pipe. Bleeding the autoclave atmosphere was done through a water-jacketed pipe to condense the water vapors back in the autoclave. Each test was done with 240 pounds of ore and 160 pounds of water.

| | ison Mines Limited, |
|-------------------------------|---------------------|
| Uranium | Ore, per cent |
| U ₃ O ₈ | 0.12 - 0.15 |
| CO2 | 0.06 |
| S total | 2.54 - 3.45 |
| SO_4/S | 0.03 - 0.18 |
| Fe | 3.11 - 3.45 |
| Rare earths | 0.25 |

In the first and second series of tests, the autoclave atmospheres were originally made up with compressed air and nitrogen and contained pre-determined amounts of oxygen, nitrogen and water vapors at 302°F. The autoclave pressures were maintained respectively, at 100 and 150 psig using compressed air supplied from a gas cylinder. The oxygen content of the bleed was determined with a Beckman Oxygen Analyzer and was frequently verified with an Orsat apparatus. The flow rate of the gas bleed was measured with a flow meter and was controlled manually so as to maintain the desired oxygen content in the bleed. The pulp was sampled every hour.

In the third series of tests, the autoclave was initially pressurized with compressed air, but for the duration of the tests, the pressures and oxygen concentrations were maintained by adding compressed oxygen. This procedure permitted the study of the effects of using oxygen partial pressures up to 19 psia without the high rate of bleed that would be required to obtain these oxygen pressures had only compressed air been introduced. Oxygen partial pressures greater than 19 psia were not investigated since the autoclave was not considered to be safe at high oxygen partial pressures.

RESULTS

The results of this test work done in the 50-gallon autoclave are shown in Table 2 and Figure 1. In tests 1 to 7 the oxygen required for the reactions was supplied as compressed air. In Figure 1, two data points are plotted for each of these 7 tests, one showing the compressed-air flow rate (solid circles) and the other showing the amount of oxygen consumed during the reactions. The per cent oxygen in the bleed is based on dry depleted air. Since the total absolute pressure in the autoclave is made up mainly of water vapour, nitrogen and oxygen, the absolute partial pressure of the oxygen in the autoclave is approximately equal to: $(P_t - P_{H_20}) \times \%_2$

Where $P_t = \text{total}$ absolute pressure in the autoclave $PH_2O = \text{absolute pressure of water vapors at 302°F.}$ (all tests were done at this temperature) $\%O_2 = \text{per cent oxygen in bleed.}$

In the first series of three tests, which are numbered 1, 2 and 3 in Figure 1, the autoclave pressure was maintained at 100 psig with compressed air, and the bleeds were adjusted to contain respectively 4.5, 7.2 and 11.9 per cent oxygen.

| Table | 2 |
|-------|----------|
|-------|----------|

| | | | | | | | Oxygen |
|------|---|----------------------|----------|----------------------|------------------|----------|---------|
| Test | the second se | r Used | Dry Oxyg | en Used | Gas Bl | Consumed | |
| No. | 1b/ | cu ft/ | 1b/ | cu ft/ | cu ft/ | ton ore | cu ft/ |
| | ton ore | ton ore ¹ | ton ore | ton ore ² | Wet ³ | Dry | ton ore |
| 1 | 36.17 | 488 | | | 433 | 419 | 68 |
| 2 | 79.63 | 1077 | | | 904 | 876 | 201 |
| 3 | 249.20 | 3370 | | | 3132 | 3034 | 336 |
| 4 | 102.20 | 1383 | | | 1181 | 1144 | 239 |
| 5 | 146.40 | 1980 | | | 1738 | 1684 | 296 |
| 6 | 217,50 | 2942 | | - | 2574' | 2493 | 449 |
| 7 | 314.80 | 4260 | | | 3840 | 3720 | 540 |
| 8 | | | 57.9 | 708 | | | |
| 9 | | | 69.4 | 849 | | | |
| 10 | | | 84.2 | 1031 | | | |

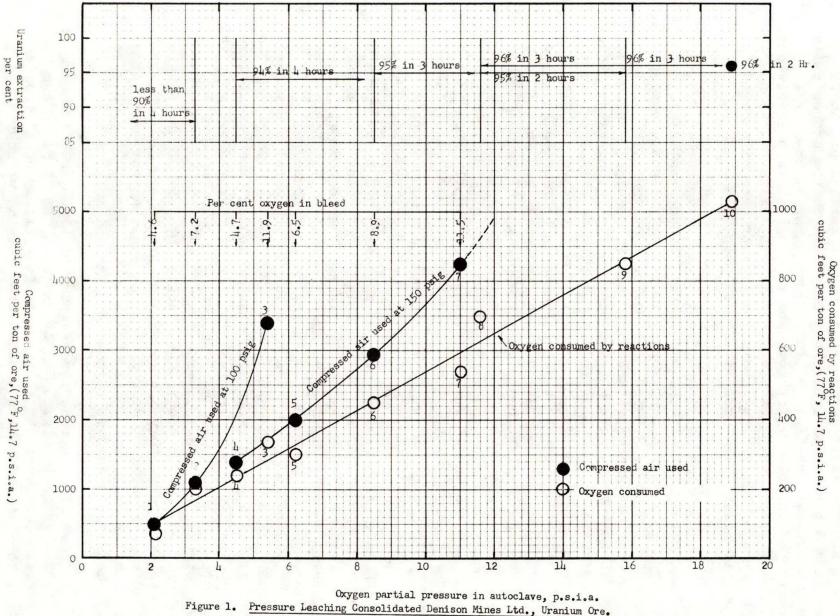
Records of Dry Air and Oxygen Used and Dry Bleed Measurements During 4-hour Leaching Periods

1 - Calculated using 0.07394 lb/cu ft as the density of air at 77° F, atmosphere (4)

2 - Calculated using 0.08172 lb/cu ft as the density of oxygen at 77° F, 1 atmosphere (4)

3 - The gas bleed flow was measured at $77^{\circ}F$ and the bleed was saturated with water vapor at that temperature. The O₂ content of the bleed was measured on a sample of dried air.

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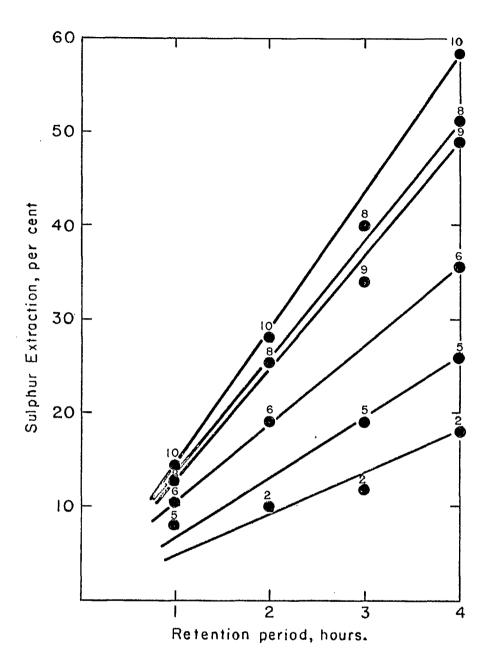


Relationship between uranium extraction rates, compressed air used and oxygen consumed by reactions in the autoclave with oxygen partial pressure. Conditions: temperature, 302°F; pulp density, 60 percent solids; ore size, 85 per cent minus 200 mesh; duration of tests, 4 hours. ו נו Tests 1, 2 and 3, Figure 1, show that oxygen partial pressures greater than 5.5 psia (11.9 per cent O_2) could not be economically obtained with compressed air at 100 psig because of the very high volume of gas bleed that would be needed with such conditions. Consequently, the uranium extraction rate was limited to 94 per cent in 4 hours, and it appeared unlikely that this rate could be increased using compressed air at 100 psig.

In the second series of tests, which are numbered 4, 5, 6 and 7 in Figure 1, the autoclave pressure was maintained at 150 psig, again with compressed air, and the bleeds contained respectively 4.6, 6.5, 8.9 and 11.5 per cent oxygen. The maximum air bleed that could be obtained with the test equipment used was achieved in test 7, and attempts to operate the autoclave at higher flow rates so as to obtain a bleed of greater than 11.5 per cent oxygen, resulted in the gas pressure in the autoclave dropping to less than 150 psig. The best rate of uranium extraction achieved in the test work with compressed air at 150 psig, was 95 per cent in three hours. However, based on extrapolation of the data obtained at 150 psig (Figure 1), it appeared likely that higher rates of extraction could be achieved with suitably designed equipment by operating at air-flow rates sufficiently high that an oxygen partial pressure of about 13 psia would be maintained in the autoclave.

Based on tests 4 to 7, it appeared unlikely that rates of uranium extraction greater than 96 per cent in 3 hours could be achieved with compressed air at 150 psig. Consequently, a third series of tests (Tests 8, 9 and 10, Figure 1) were done with the atmosphere in the autoclave being maintained at 11.7, 15.8 and 19.0 psia oxygen respectively by adding compressed oxygen instead of compressed air to the autoclave. The total pressures in tests 8, 9 and 10 were respectively 100, 150 and 175 psig. The maximum rate of uranium extraction obtained under these conditions was 96 per cent in 2 hours in test 10. There was evidence that this extraction was close to the maximum possible. A mineralogical analysis of the leach residue from test 10 revealed that most of the undissolved uranium occured as brannerite, part of which was intergrown with refractory minerals, and which could not be extracted without further grinding. A small amount of uranium also occurs in monazite which is known to be refractory under the leaching conditions used in this work.

The sulphur extractions versus leaching times for some of the tests are shown in Figure 2. As expected, these plots are about linear because of the short retention periods used, indicating that the rates of sulphur extraction were about constant throughout the leaching.



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Figure 2. Pressure Leaching Consolidated Denison Mines Ltd. Uranium Ore. Sulphur Oxidation to Sulphate.

Table 3 shows a summary of the process heat required in pressure leaching an Elliot Lake uranium ore similar to the sample used in this work with either compressed air or oxygen. The details of the calculations are compiled in Appendices A and B.

Table 3

Summary of the Process Heat Required in Pressure Leaching a Uranium Ore With Compressed Air or Oxygen

| | | Compressed air | |
|----------------------|-------------|----------------|------------|
| | | (Figure 1, | (Figure 1, |
| · | | Test 6,) | Test 8.) |
| Heat to ore, water | | | |
| air or oxygen | BTU/ton ore | 403,422 | 396,940 |
| Heat removed as | | | |
| steam to bleed | | | |
| condenser, | BTU/ton ore | 51,493 | |
| | | 454,915 | 396,940 |
| Deduct the heat of | | | |
| reactions | BTU/ton ore | 143,986 | 291,363 |
| Net heat required | BTU/ton ore | 310,929 | 105,577 |
| Fauivalant cost of | fuel oil | | |
| Equivalent cost of | = | | |
| | \$/ton ore | 0.358 | 0.121 |
| 185,000 BTU/imp.ga | llon, | | |
| \$0.16 per imp. gall | lon | | |
| steam generation et | ffc'y, 75% | | |
| | | | |

DISCUSSION

The data, based on the results of this work and shown in Figure 1, provide a wide range of conditions that will result in greater than 94 per cent extraction of the uranium from Elliot Lake ore by acid-pressure leaching methods. For example, 94 per cent of the uranium can be extracted in 4 hours at a total pressure of 100 psig, a temperature of 302° F, and an oxygen partial pressure of about 4 psi absolute. At the other end of the scale it is foreseen that 96 per cent of the uranium can be extracted in 2 hours at a total pressure of about 73 psig, (69.04 psia H₂O + 19 psia O₂) a temperature of 302° F, and an oxygen partial pressure of 19 psi absolute. This latter set of conditions could be obtained, economically only by using compressed oxygen rather than compressed air.

The cost of the process heat and of the oxygen consumed while supplying either compressed air or compressed elemental oxygen under several sets of conditions chosen from Figure 1, were calculated and are given in Table 4. It was assumed for these calculations that the maximum possible uranium extraction Where a set of conditions gave less than 96 was 96 per cent. per cent extraction, the difference was charged as a cost to the Although the cost of compressed air is much lower than process. that of compressed oxygen, this advantage is partially off-set by a lower process-heat cost with compressed oxygen because no Detailed calculations gas bleed is needed with compressed oxygen. are given in Appendices A and B.

As Table 4 shows, the lowest cost of acid-pressure leaching of ore similar to the sample of Denison ore, used in this work, would be about \$0.39 per ton of ore. This cost would result from treating the ore at 302°F, at a total pressure of 150 psig, and an oxygen partial pressure of 11.0 psia, for three hours, and using compressed air to supply the required oxygen. The uranium extraction would be 95 per cent. Actually, as is shown in Table 4 a wide range of conditions costing in the range of \$0.39 and \$0.57 per ton of ore will give 95-96 per cent extraction. Which set of conditions will be the least costly will depend on the actual costs of compressed air or oxygen, heat, and the uranium - recovery loss in any given operation.

Table 4

Cost of Reagents and Uranium-Recovery Loss in Pressure Leaching a Uranium Ore with Compressed Air or Oxygen

| | | • | | | | | | | |
|------|----------|-------|--------|-----------|---------|----------|---------|----------|---------|
| Test | | Urani | | Autoclave | | t of Rea | | Uranium- | |
| NO. | | | lction | Pressure | Air* | | Process | | |
| | Pressure | Rate | ······ | | | | Heat*** | | |
| | psia | % | hr | psig | \$/ | \$/ | \$/ | \$/ | \$/ |
| | | | | | ton ore | ton ore | ton ore | ton ore | ton ore |
| 1 | 2.1 | 85 | 4 | 100 | 0.005 | | 0.432 | 0.924 | 1.361 |
| 2 | 3.3 | 88 | 4 | 100 | 0.012 | | 0.458 | 0.672 | 1.142 |
| 3 | 5.5 | 94 | 4 | 100 | 0.038 | | 0.637 | 0,168 | 0.843 |
| 4 | 4.4 | 94 | 4 | 150 | 0.019 | | 0,366 | 0.168 | 0.553 |
| 5 | 6.2 | 94 | 4 | 150 | 0.029 | | 0.337 | 0.168 | 0.534 |
| 6 | 8.5 | 95 | 3 | 150 | 0.031 | | 0.359 | 0.084 | 0.474 |
| 7 | 11.0 | 95 | 3 | 150 | 0.045 | | 0.264 | 0.084 | 0.393 |
| 8 | 11.7 | 95 | 2 | 100 | | 0.197 | 0.247 | 0,084 | 0.528 |
| 8 | 11.7 | 96 | 3 | 100 | | 0.296 | 0.121 | - | 0.417 |
| 9 | 15.8 | 95 | 2 | 150 | • | 0.236 | 0.247 | 0.084 | 0.567 |
| 9 | 15.8 | 96 | 3 | 150 | | 0.353 | 0.172 | - | 0.525 |
| 10 | 19.0 | 96 | 2 | 175 | | 0.288 | 0.222 | | 0.510 |

* Refer to Appendix C for cost of air.

** Cost of Compressed oxygen, \$15.00 per ton (8).

*** Sample calculations shown in Appendices A and B.

**** 2.5 1b U₃O₈ per ton of ore; basic cost of mining and milling, \$8.40 per ton of ore; maximum uranium recovery, 96 per cent.

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions made to this work by other members of the Extraction Metallurgy Division. Mr. S. Poulin conducted the test work. The analytical work was carried out under the direction of Messrs J.C. Ingles and J.B. Zimmerman. Mr. S. Kaiman, head of the Mineralogical Section directed the mineralogical analysis of a leach residue. Thanks are also expressed to Mr. H.W. Smith, Division Planning Officer, for providing cost figures to the authors.

APPENDIX A

HEAT CALCULATIONS FOR THE PRESSURE LEACHING OF DENISON ORE WITH COMPRESSED AIR (TEST 6, FIGURE 1)

The calculation of the heat requirements for the acid pressure leaching of Denison ore under the conditions used in Test 6, Figure 1 were based on the following considerations:

(a) The autoclave would be operated at 150 psig and 302°F, and the ore would be leached under these conditions for 3 hours (Table 4) as a slurry containing 60% solids by weight.

(b) The temperature of the air, water and ore entering the autoclave would be 77° F. The line pressure of the air inlet pipe would be just slightly above the autoclave working pressure so that any cooling due to expansion in the autoclave would be negligible.

(c) Oxygen depleted air could be bled to atmosphere (14.7 psia) from the autoclave through a condenser where it would be cooled to 77° F, and thus the water condensed in cooling from 302° F to 77° F would remain in the autoclave. The cooled air would then be released to atmosphere (14.7 psia) and therefore would have no effect on the temperature of the autoclave contents.

(d) Ore, water, air and heat would be added to and removed from the autoclave continuously at constant rates.

(a)

Since the heat capacity of the ore was not known, the following heat capacity of quartz, as calculated from published heat content data⁽⁵⁾was used as the heat capacity of the ore in this calculation.

 $H_{400}-H_{77}$ (quartz) = 4060 BTU/lb - mole⁽⁵⁾ = $\frac{4060}{60}$ = 67.6 BTU/lb.

Average heat capacity of quartz between $77^{\circ}F$ and $400^{\circ}F$ is therefore:

 $\frac{67.6}{400-77} = 0.21 \text{ BTU/lb/°F.}$

Heat required to raise 2000 lbs. of ore from $77^{\circ}F$ to $302^{\circ}F$ is

 $2000 \times 0.21 \times (302-77) = 94,500 \text{ BTU/ton of ore}$.

(b) <u>Heat required to heat water from 77°F to 302°F</u>

One ton of ore requires 1,333 lbs water to produce a slurry containing 60% solid by weight. The heat required to heat this water from 77° F to 302° F is

 $1,333 \times 1 \times (302-77) = 300,000 \text{ BTU/ton ore}$.

(c) <u>Heat required to heat air from 77°F to 302°F at constant</u> <u>Pressure of 150 psig and essentially constant volume in</u> <u>the autoclave</u>

The volume of dry air used in Test 6 was 2,942 cu ft/ton of ore over a 4-hour leaching period (Table 2). The extraction reached a value of 95% in 3 hours and did not increase during the last hour of leaching. Finally, the rate of sulphur extraction during leaching was found to be practically linear (Figure 2). Therefore it was assumed that the amount of air needed for the required 3-hour leaching period would be three-quarters of that used in the 4-hour leach reported (Test 6) or 2207 cu ft/ton of ore. Density of dry air at 14.7 psia and $77^{\circ}F = 0.07394$ lb/cu ft(4). Volume of dry air required = 2,942 x $\frac{3}{4}$ = 2,207 cu ft/ton ore. and weight of dry air required = 2,207 x 0.07394 = 163.18 lb/ton ore. Heat capacity of air (Cp)at 150 psig = 0.243 BTU/lb/°F. Therefore heat required to increase air temperature from $77^{\circ}F$ to $302^{\circ}F = 163.18 \times 0.243 \times (302-77) = 8922$ BTU/ton ore.

(d) Heat Required to Vaporize Water Present in Gas Bleed

Since, as argued above, the volume of air to the autoclave is assumed to be 3/4 of the volume shown in Table 2, it follows that the volume of saturated air at $77^{\circ}F$ and 14.7 psia discharged from the condenser per ton of ore would be $\frac{3}{4}$ of the measured volume given in Table 2.

Volume of water-saturated air at 77°F and 14.7 psia discharged from autoclave = $2574 \times \frac{3}{4} = 1930$ cu ft/ton ore.

Volume of dry air discharged from autoclave at 77°F and 14.7 psia = $1930 - 1930 \times \left\{ \begin{array}{c} 0.46 \\ 14.7 \end{array} \right\}$ = 1870 cu ft/ton ore, where the vapor pressure of the water at 77°F is 0.46 psia(4).

The partial pressure of dry air at $77^{\circ}F$ and 14.7 psia = 14.7 - 0.46 = 14.24 psia.

The vapour pressure of steam at $302^{\circ}F = 69.01$ psia(4).

Therefore the volume of dry air bled from the autoclave per ton of ore treated when at the operating temperature $(302^{\circ}F)$ and pressure (164.7 psia) of the autoclave.

 $= 1870 \times \frac{14.24}{164.7 - 69.01} \times \frac{460+302}{460+77} = 395 \text{ cu ft.}$

The volume of water vapors carried to the condenser by this volume of air

 $= 395 \times \frac{69.01}{95.69} = 285 \text{ cu ft},$

and the weight of water carried as steam to the condenser by the air

= $285 \times 0.1592 = 45.4$ lb/ton of ore treated, where 0.1592 is the weight of 1 cu ft of water vapor at 302° F and 150 psig

Most of the heat in this amount of water (45.4 lb/ton of ore) at $302^{\circ}F$ is lost, partly due to the cooling in the condenser and partly in the water vapor released from the condenser at $77^{\circ}F$. This amount of heat is equivalent to the heat required to heat the water from $77^{\circ}F$ to $302^{\circ}F$ plus that required to vaporize the water and equals:

| $45.4 \times 226.8 (4) =$ | 10,297 |
|---------------------------|--------------------|
| $45.4 \times 907.4 (4) =$ | 41,196 |
| Total | 51,493 BTU/ton ore |

(e) Total Heat Required for Items (a) to (d)

| Heat | required | for | ore = | 94,500 | BTU/ton ore |
|------|----------|-----|--------------------------|---------|-------------|
| Heat | required | for | water added in the ore = | 300,000 | BTU/ton ore |
| Heat | required | for | air added with ore = | 8,922 | BTU/ton ore |
| Heat | required | for | steam lost in air bleed= | 51,493 | BTU/ton ore |
| | | | Total | 454,915 | BTU/ton ore |

Heat Credit From Exothermic Oxidation of Contained Pyrite

These calculations are based on analyses of solution and residue. These analyses showed that 27% of the original 2.54% sulphur present in the ore as sulphide was oxidized in 3 hours (Figure 2). The distribution of the oxidized sulphur shown in the following table assumes all of the oxidized sulphur in the leach solution and residue is there as ferric or ferrous sulphate, sulphuric acid and basic ferric sulphate.

| Distribution of Oxidized Sulphur in Reaction Products | | | Assumed Reactions (The bracketed values represent 1b S/ton ore) |
|---|---------------|-----------------------------|--|
| Product | % | lb/ton of ore treated | |
| Solution | | | |
| FeSO4 H ₂ SO ₄ | 13.9 43.2* | 1.904 5.920 | $\begin{array}{rl} 2 \mathrm{FeS}_{2} + 70_{2} + 2 \mathrm{H}_{2} \mathrm{O} & 2 \mathrm{FeSO}_{4} + 2 \mathrm{H}_{2} \mathrm{SO}_{4} & (\mathrm{Eq} \ 1) \\ (13.7) & (6.85) & (6.85) \end{array}$ |
| Fe ₂ (SO) ₃ | 21.1 | 2.890 | 2FeSO ₄ + H ₂ SO ₄ + $\frac{1}{2}$ O ₃ Fe ₂ (SO ₄) ₃ + H ₂ O (Eq 2) (4.946) (2.473) (7.419) |
| Residue | | | |
| | | | $ \begin{array}{c} Fe_{g}(SO_{4})_{3} + 6H_{2}O & 2Fe(OH)_{3} + 3H_{2}SO_{4} & (Eq 3) \\ (0.05) & (0.05) \end{array} $ |
| Fe(OH). SO ₄ .H ₂ O | 21.8 | 2.986 | $Fe_2(SO_4)_3 + 4H_2O$ $2Fe(OH)SO_4 \cdot H_2O + H_2SO_4(Eq 4)$ (4.479)(2.986)(1.493) |
| Total | 100.0 | 13.7 | |

* by difference

1

| FeSz | - 35,500 | cal / | gram-n | ole |
|--|----------|-------------|--------|-----------|
| H ₂ O | - 68,370 | 11 11 | ** | 11 |
| Fe(OH) ₃ | -197,400 | TT . | 11 | 11 ' |
| $H_2 SO_4$ | -212,400 | 11 . | 11 | 11 |
| $\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3}$ | -653,000 | ** | 11 | 11 |
| FeSO4 | -236,000 | 11 | ** | ** |
| $Fe(OH)SO_4H_2O$ | -394,870 | 11 | 11 | ** |

Heats of Formation of Reactants and Products (10)

The heat of formation of $Fe(OH)SO_4H_2O$ could not be found in the literature. The figure above is that of $Fe_2(SO_4)_3$ plus the heat of formation of water.

Based on the equations, material balances and heats of formation given above, the following calculations of the heat generated by the oxidation of pyrite were made:

| Eq. | 1 | -689,060 x 1.8 | | 1 | 32,500 | BTU/ | ton | ore |
|-----|---|----------------|---------------------------------|------------|--------|------|-----|----------------|
| Eq. | 2 | - 36,970 x 1.8 | $ x \frac{7.419}{3 x 32} $ | — — | 5,140 | ** | 11 | 11 |
| Eq. | 3 | + 31,220 x 1.8 | | ≕ + | 29 | 11 | 11 | 11 |
| Eq. | 4 | - 75,660 x 1.8 | $ x \frac{4.479}{3 \times 32} $ | ш н | 6,375 | tt | 11 | |
| | | Tot | al | -1 | 43,986 | BTU/ | ton | \mathbf{ore} |

Cost of Heat Required by Leaching Reaction

| Total heat required | Ħ | 454,915 | BTU/ton | ore |
|--------------------------------------|---|---------|---------|-----|
| Heat credit from oxidation of pyrite | = | 143,986 | 11 11 | 11 |
| Net heat required | - | 310,929 | BTU/ton | ore |

On the basis that one Imperial gallon of fuel oil costs \$0.16, and has a heat equivalent of 185,000 BTU, and that the steam generator recovers 75% of the heat from the oil, the above heat requirement would cost:

 $\frac{310,929}{0.75 \times 185,000} \times 0.16 = \$0.358/ton \text{ ore }.$

Items Not Considered in Above Heat Balance

Some of the more obvious items not considered in the above calculation are as follows:

(a) The radiation losses from the leaching vessel and auxiliary equipment.

(b) No correction was made for the fact that the reactions would be done at 150° C while the heats of formation used are those at 18° C.

(c) No corrections were made for the fact that the heat of formation used were based on the product being in the solid state while in the system considered here, some of the products are in solution.

Item (a) was neglected because it would depend on the design of the autoclave and an assumed value would have no real meaning. Items (b) and (c) were neglected since the error arising from their exclusion would be less than the difference that could be obtained by using heats of formation from different references.

Because of the exclusion of some of the heat considerations, the heat requirement calculated is probably low but by not more than 10 per cent.

APPENDIX B

HEAT CALCULATIONS FOR THE PRESSURE LEACHING OF DENISON ORE WITH OXYGEN (TEST 8, FIGURE 1)

The calculations of the heat requirements for the acid pressure leaching of Denison ore under the conditions used in Test 8, Figure 1 were based on the same considerations as those used in Appendix A for leaching with compressed air with the following exceptions.

(a) Oxygen at 77°F, instead of compressed air, would be introduced to the autoclave at its operating pressure.

(b) Since only oxygen would be added, there would be no need to bleed gases from the autoclave.

(c) The operating pressure of the autoclave would be 100 psig instead of 150 psig as used with compressed air.

Process Heat Requirements for Ore Ton of Ore Treated

(a) Heat required to heat ore and water from $77^{\circ}F$ to $302^{\circ}F$

The heat required to heat the ore and water added to the autoclave to 302°C is, of course, the same as that needed when compressed air is used and is as calculated in Appendix A.

Heat for ore and water = 394,500 BTU/ton ore.

(b) Heat required to heat oxygen from 77°F to 302°F at constant pressure of 100 psig and essentially constant volume in the autoclave

The volume of oxygen used in Test 8 was 708 cu ft/ton (Table 2). The results of Test 8 showed that the uranium extraction after 3 hours was 96% and that it was not increased further after 4 hours. The rate of sulphur extraction in test 8 was shown to have been about linear (Figure 2). It thus appeared reasonable for the purpose of calculations that a retention of 3 hours would be sufficient and that the oxygen required would be $\frac{3}{4}$ of the volume recorded for Test 8, Table 2.

Density of O_g at 14.7 psia and $77^\circ F = 0.08172$ lb/cu ft (4). O_g requirement for 4 hours for test 8, Table 2 = 708 cu ft/ton ore. O_g requirement for 3 hours = 708 x 0.75 = 531 cu ft/ton ore, or 531 x 0.08172 = 43.39 lb O_g /ton of ore treated.

Heat capacity of O_2 at $302^{\circ}F = 0.229 \text{ x} (302-77) = 2440 \text{ BTU/ton}$

(c) Total Heat Required for Items (a) and (b)

| Heat | required | for | ore and | water | - | 394,500 | BTU/ton | ore |
|------|----------|-----|---------|-------|---|---------|---------|-----|
| Heat | required | for | oxygen | | = | 2,440 | TT 11 | 11 |
| | | | Tot | al | = | 396,940 | BTU/ton | ore |

Heat Credit from Exothermic Oxidation of Contained Pyrite

In calculating the heat credit due to the reactions, only the oxidation of pyrite was considered. The analyses of the reaction products showed that 40% of the original 3.45% sulphur was oxidized at the higher oxygen partial pressures obtained when oxygen only was added to the autoclave.

| Distribution | of | the | Oxidized | Sulphur | in | Reaction | Products |
|--------------|----|-----|----------|---------|----|----------|----------|
| | | | | | | | |

| Sulphur Distribution | | | Assumed Reactions | | | | |
|-------------------------------------|--------|----------|---|--|--|--|--|
| Products Solution | % | lb/t ore | (The bracketed values represent 1b S/ton ore) | | | | |
| | | | | | | | |
| FeSO | 13.5 | 3.73 | $2 \text{FeS}_2 + 7 \text{ O}_2 + 2 \text{H}_2 \text{O} 2 \text{FeSO}_4 + 2 \text{H}_2 \text{SO}_4 \text{eq. 1}$ | | | | |
| $H_{2}SO_{4}$ | 48.6 | 13.41 | (27.6) (13.8) (13.8) | | | | |
| | | | | | | | |
| Fe ₂ (SO ₄); | 13.7 | 3.78 | $2 \text{FeSO}_4 + H_2 SO_4 + \frac{1}{2}O_2$ Fe ₂ (SO ₄) ₂ + H ₂ O eq. 2 | | | | |
| | | | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | | | | |
| | | | | | | | |
| Residue | | | | | | | |
| | | | $\begin{array}{rll} & \operatorname{Fe}_{\varkappa}(\operatorname{SO}_{4})_{3} + 6 \operatorname{H}_{2}\operatorname{O} & 2 \operatorname{Fe}(\operatorname{OH})_{3} + 3\operatorname{H}_{3}\operatorname{SO}_{4}, & \operatorname{eq.} 3 \\ & (1.305) & & (1.305) \end{array}$ | | | | |
| Fe (OH) SO | | | | | | | |
| II ₂ O | 4.24.2 | 6.68 | $Fe_3(SO_4)_3 + 4H_2O$ $2Fe(OH)SO_4.H_2O + H_2SO_4,eq.4$ (10.02)(6.68) | | | | |
| Total | 100.0 | 27.60 | | | | | |

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* by difference.

Based on the equations and material balances given above and the heats of formation listed in Appendix A, the following calculations of the heat generated by the oxidation of pyrite were made:

| (Eq 1) | -689,060 x 1.8 x $\frac{27.6}{4 \times 32}$ | = | - 267,441 BTU/ton ore |
|--------|---|---|----------------------------|
| (Eq 2) | - 36,970 x 1.8 x $\frac{15.105}{3 \times 32}$ | = | - 10,470 BTU/ton ore |
| (Eq 3) | + 31,220 x 1.8 x $\frac{1.305}{3 \times 32}$ | = | + 764 BTU/ton ore |
| (Eq 4) | - 75,660 x 1.8 x $\frac{10.02}{3 \times 32}$ | = | - 14,215 BTU/ton ore |
| | Total | - | 291,363 BTU/ton ore |

Cost of Heat Required by Leaching Reaction

| Total heat required | = | 396,940 | BTU/ton | ore |
|---------------------|---|---------|---------|-----|
| Heat credit from | | | | |
| oxidation of pyrite | = | 291,363 | BTU/ton | ore |
| Net heat required | | 105,577 | BTU/ton | ore |

On the basis that one Imperial gallon of fuel oil costs \$0.16 and has a heat equivalent of 185,000 BTU, and that the steam generator recovers 75% of the heat in the oil, the above heat requirement would cost

 $\frac{105,577}{0.75 \times 185,000} \times 0.16 = \0.121

Items not Considered in Above Balance

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The same comments under the heating in Appendix A apply here.

| Pressure | Power pe | r 1,000 cfm | Unit cost | Cost per 1,000 cu ft |
|----------|----------|-------------|-----------|----------------------|
| psig | hp | kWh | \$/kWh | dollars |
| 100 | 180 | 2.24 | 0.005 | 0.011 |
| 150 | 220 | 2.75 | 0.005 | 0.014 |
| 175 | 240 | 2.98 | 0.005 | 0.015 |

Approximate cost of power to compress air (6,7)

