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RECOVERY OF COBALT FROM TAYLOR GEM ORE
BY AQUEOUS OXIDATION.

by

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ABSTRACT.

The problem of recovering cobalt from a cobalt arsenide ore in caustic, ammonia, and water solutions, all under oxygen pressure, has been examined. A wide range of temperatures and pressures were used to produce either a soluble or an insoluble oxidized form of cobalt. Subsequent treatment of certain oxidized residues included sulphuric acid and caustic leaching, and ammonium hydroxide leaching under hydrogen pressure.

A general outline of the ore treatment in all the above solutions is presented to indicate the course of the research and to show why certain procedures were used.

Consideration is then given separately to the experimental work in each of the solutions with regards to equipment, procedure and results. In each case a discussion of the results is given together with free energy calculations which justify some of the conclusions.

Caustic treatment of the ore proved difficult but both ammonia and water treatment showed good possibilities for commercial development. In caustic solution, oxidation of the ore followed by a hot, 25% sulphuric acid leach extracted only 70% cobalt. In ammoniacal solution the cobalt was oxidized completely to the residue and 95% of it was then leached in hot, dilute sulphuric acid but solution contamination by arsenic was serious. In water solutions between 85% and 90% of the cobalt was recovered directly in a fairly pure solution provided enough iron was present as pyrite to precipitate the arsenic.

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PART 1: INTRODUCTION.

In recent years, several research projects related to the Metallurgy of the Taylor Gem ore have been carried out in the Department of Mining and Metallurgy at the University of British Columbia. The ore is a complex mixture of cobalt-iron arsenides and arsenophyrite with varying values of gold and uraninite. Conventional roasting and leaching methods have been used to recover the cobalt, as well as variations such as the reduction of the roasted ore with hydrogen followed by ammonium, ammonium sulphate leaching. In any treatment involving roasting or sintering great care must be taken to prevent the formation of ferrites, or the fusion of calcine particles, both of which reduce cobalt recovery.

Recent investigations have been carried out in the Department on the leaching and oxidation of ores in aqueous solutions under oxygen pressure. Forward and his associates ⁽¹⁾ have reported that copper and nickel may be leached directly from a sulphide ore in ammonium hydroxide solutions under oxygen pressure. The copper and nickel remain in solution as the slightly dissociated complex amines while the iron remains in the residue. Satisfactory precipitation of the copper and

(1) Forward, F.A., Samis, C.S., Kudryk, V., "A Method for Adapting the Ammonia-Leaching Process to the Recovery of Copper and Nickel from Sulphide Ore and Concentrate", Canadian Mining and Metallurgical Bulletin, 434, 350-355 (1948).

(2)
nickel could be obtained. Carter reported that good gold recoveries could be obtained from a refractory gold ore by first oxidizing the ore in caustic solution under oxygen pressure, followed by ordinary cyanidation procedure. By oxidizing the ore in solution the temperature rise of the individual sulphide particles was limited to such an extent that no fusion took place.

The present work was undertaken in an effort to determine whether the Taylor Gem ore could be leached or oxidized in aqueous solution under oxygen pressure so that the cobalt would remain in solution or be easily recoverable from the residue.

- (2) Carter, R., "The Influence of Roasting Temperature upon Gold Recovery from a Refractory Gold Ore", Master's Thesis, University of British Columbia, 1949.

PART 2: MINERALOGY OF THE ORE AND DESCRIPTION OF MATERIALS.

The investigation described in this paper was carried out on a cobalt-gold ore, submitted by Mr. R. R. Taylor, from the Taylor Gem Mine. The ore so far disclosed consists of a mixture of arsenopyrite (FeAsS); dainite (CoFeAsS), and loellingite-safflorite ($\text{CoAs}_2\cdot\text{FeAs}_2$), with a little molybdenite in a gangue of quartz, feldspar, and altered country rock. Extremely fine gold particles are distributed irregularly throughout both dainite and loellingite-safflorite and have been observed in the associated gangue minerals. (3) Varying amounts of uraninite containing commercial values of uranium, have been discovered and have led to a more active interest in the mine.

Initially the material used was a composite concentrate, supplied by Mr. R. R. Taylor, of the following composition:

Co 2.41%	S 12.1%	MgO 0.6%
Fe 23.5%	CaO 0.9%	Al_2O_3 6.3%
As 32.5%	SiO_2 14.0%	Au 1.8 oz/ton.

Later Mr Taylor supplied several hundred pounds of high-grade, hand-picked cobalt-gold ore and over a hundred pounds of hand-picked uranium ore. About twenty pounds of the latter were mixed with over a hundred pounds of the cobalt ore to produce a new head sample, GM-200, having the following composition:

- (3) Warren, H.V., Thompson, R.M. "Mineralogy of Two Cobalt Occurrences in British Columbia", Western Miner, PP. 34-41, May, 1945.

GM-200

Co 6.0%

S 8.5%

Fe 22.0%

Au 0.96 oz/ton

As 44.7%

U_3O_8 0.02%

Most of the experimental work was done on the GM-200 head sample.

A very limited number of tests were made on two calcines
(4)
produced by Taylor.

#1 Calcine.

Co 7.7%

As 6.2%

Fe 32.4%

S 1.26%

SiO_2 22.0%

CaO 1.9%

#2 Calcine.

Co 8.04%

As 4.0%

Fe 33.4%

S 0.55%

- (4) Taylor, R.R., "An Investigation of Treatment Methods of Cobalt Ore from the Gem Mine Bridge River", Master's Thesis, University of British Columbia, 1941.

PART 3: SUMMARY OF EXPERIMENTAL WORK AND GENERAL RESULTS.

1. Oxidation in Caustic Solutions.

(5)

Calculations by Carter indicate that the driving force for the oxidation of a sulphide ore was greater in caustic than in neutral solutions. Tests were therefore carried out in 18N, 6N, and 3N caustic solutions at temperatures and pressures ranging from 220 - 405°F and 200 - 210 psig. All results are summarized in Table 1, Part 4.

The important results obtained in 18N caustic solutions were as follows:

- (a) Up to 34% of the cobalt was recovered from the composite concentrate as the soluble cobaltite. This was obviously an equilibrium product because at longer oxidizing times all the cobalt appeared in the residue as the oxide or hydroxide.
- (b) By repeated oxidation of GM-200 a maximum of 50% cobalt was recovered. Oxidation was very slow and even at high temperatures was never completed.

In view of the low cobalt recoveries as an equilibrium product, and slow oxidation of the ore, the concentrated caustic leaches were discontinued. The low rate of oxidation was attributed to the low solubility of oxygen in strong caustic solutions.

(5) Carter, "Gold Recovery", Master's Thesis (1949).

Consequently, the next tests were made in 6N and 3N solutions.

The important results obtained in these solutions were as follows:

- (a) The ore was readily oxidized with all the cobalt going to the residue as the oxide or hydroxide.
- (b) No appreciable difference was noted in the rate of oxidation in 6N and 3N caustic.

Various leaching procedures were then tried to recover the cobalt from the above mentioned residues. Complete results are given in Tables 2 and 3, Part 4. The important results are as follows:

- (a) No cobalt was leached from the residue in concentrated ammonium hydroxide.
- (b) Up to 40% was recovered in ammonium hydroxide leaches under gaseous hydrogen pressure.
- (c) Various acid leaches were ^{tried} with a maximum recovery of 70% being obtained in hot, 25% sulphuric acid.

As these results showed rather poor possibilities, caustic treatment of the ore was discontinued and full attention was turned to ammonia treatment.

2. Oxidation in Ammoniacal Solutions.

(6)

Forward and his associates reported that copper and nickel

(6) Forward, "Ammonia-Leaching Process", C.M.M.B. 434 350-355.

could be leached by ammonium hydroxide from a sulphide ore at low temperatures under 30 psig O_2 pressure. To determine if cobalt could be similarly leached from an arsenide ore, tests were carried out at 70 - 115°F and 30 psig O_2 with the following results: (Details - Table 4 Part 5).

- (a) Less than 1% was recovered in solution.
- (b) There was no evidence of oxidation.

Apparently the cobalt was combined in a very stable form. Therefore, the next leaching tests were carried out at higher temperatures and total pressures, varying between 220 and 380°F and 200 to 475 psig. The results may be summarized as follows:
(Details - Table 5, Part 5).

- (a) Up to 35% of the cobalt was recovered as the complex cobalt-ammonium ion but the recovery varied with leaching time.
- (b) At long leaching times the cobalt was completely oxidized to the residue. This indicated that the soluble cobalt complex was an equilibrium product.
- (c) The color^{and} density of the residue indicated ~~that~~ cobalt and iron were combined as some form of complex arsenate.
- (d) Complete oxidation was obtained more easily in dilute than in concentrated ammoniacal solutions.

The oxidized residues produced in the above treatment were then leached in sulphuric acid with the following results:
(Details - Tables 6, 7 Part 5)

- (a) At least 70% of the cobalt was recovered in cold, 25% acid.
- (b) Up to 95% was leached in hot, 5% acid.
- (c) Contamination was serious, especially in the more concentrated acids which contained 80 - 90% of the Fe and As. In dilute acid about 25 - 30% of the Fe and As remained in solution while the balance was precipitated as the insoluble iron arsenate.

Purification experiments, involving PH adjustment of the acid solutions, were tried. Lime, sodium carbonate, and sodium hydroxide were used to neutralize the solutions. The following observations were made:

- (a) Arsenic could not be eliminated as iron arsenate without precipitating some cobalt arsenate.
- (b) If excess iron was added as ferric sulphate most of the arsenic could be eliminated.

Acid leaching^{of} ammonia oxidized residues showed very good results. However, it seemed likely that oxidation and solution of cobalt could be performed in one operation if a dilute acid solution

were used. Water oxidation of the ore was therefore examined to determine whether or not sufficient acid could be generated during oxidation to keep the cobalt in solution.

3. Oxidation in Water Solutions.

A number of oxidations were made in water solutions using GM-200 at temperatures and total pressures ranging from 210 to 350°F and 35 to 380 psig. Results were as follows: (Details - Table 10, Part 6).

- (a) Cobalt recoveries varied between 70 and 83%. These solutions contained about 30% of the arsenic and no iron.
- (b) Pyrite was added to the charge to improve cobalt recovery and reduce arsenic contamination. About 90% cobalt could then be recovered in a solution containing 3% of the arsenic.

Oxidation in water solutions therefore gave good results and merits further investigation.

PART 4: OXIDATION IN CAUSTIC SOLUTION.

1. Equipment.

An autoclave built in the Mining and Metallurgy Department by Mr. J. Stenhouse was used to make all the tests. A photograph of the apparatus appears below:



Figure 1. Autoclave for Caustic Treatment.

2. Procedure.

The charged autoclave was bolted to the rocking mechanism, heated to the desired temperature, and subjected to the required oxygen pressure. Water was passed through the U-tube to cool the unit at the end of the leach.

A standard procedure was adopted in reporting the duration of each leach. The leach began when oxygen was released into the autoclave and ended when the current was switched off. Heating and cooling times were not reported.

3. Results and Observations.

(a) Oxidation in caustic.

Table 1 on the following page summarizes all oxidations in caustic solution.

1. Tests 1 - 9 were made to determine cobalt extraction in strong caustic solutions. In the ninth test a maximum of 50% recovery was obtained.

2. The object of tests 10 to 16 was to completely oxidize the ore. Tests 10, 11 and 12 compare oxidizing rates in 18N, 6N and 3N caustic. No differentiation can be made between 6N and 3N but both are faster than 18N caustic.

3. No sulphur was left in the oxidized residues and arsenic elimination was good. The 6N and 3N residues

TABLE 1 - SUMMARY OF CAUSTIC OXIDATIONS.

Test	Ore	Normality Caustic	Temp. °F	Press. Total psig	Time hrs	% Co. Recov.	Remarks.
1	(1) C.C.	18	300	200	2	34	(2) P.O.
2	C.C.	18	300	200	5 $\frac{1}{2}$	Nil	(3) C.O.
3	C.C.	18	220	200	5	Nil	C.O.
4	GM-200	18	220	200	3	Nil	(4) N.O.
5	GM-200	18	335	200	3	10	P.O.
6	GM-200	18	360	200	3	10	P.O.
7	GM-200	18	300	200	4	10	P.O.
8	Two releaches of #7 Residue 1 hr. each.					15	P.O.
9	GM-200	18	405	210	4	15	P.O.
	Three releaches of #9 Residue for 1 $\frac{1}{2}$ hrs. each.						
	Total Co Rec.					50	P.O.
10	GM-200	18	405	210	4	15	P.O.
11	GM-200	63	405	210	2 $\frac{1}{2}$	Nil	C.O.
12	GM-200	3	405	210	2 $\frac{1}{2}$	Nil	C.O.
13	GM-200	2	190	50	7	Nil	P.O.
14	GM-200	63	405	380	15	Nil	C.O.
15	GM-200	3	405	380	15	Nil	C.O.
16	GM-200	IN.	302	375	?	Nil	C.O.

(1) Composite concentrate

(2) Partially Oxidized

(3) Apparently completely oxidized.

(4) No Oxidation.

contained 2.2 and 10.3% respectively.

4. In test 16 the rate of oxidation was measured by recording the decrease in oxygen pressure in a small tank. This showed that the oxidation approximated a first order reaction.

(b) High Pressure Hydrogen Leaches.

Caustic oxidized residues were leached under hydrogen pressure in concentrated (28%) ammonium hydroxide. The object of these leaches was to reduce cobalt hydroxide or oxide to a soluble form. A summary of the results is presented in Table 2.

Table 2. Summary of Hydrogen Leaches.

Test #	Caustic Residue Used.	% Solids	Temp. °F.	H ₂ Press psig.	Time hrs	% Co. Rec.	
1	#2	10	200	250	4	40%	10% (NH ₄) ₂ SO ₄
2	#2	10	200	250	4	30%	
3	#12	10	200	250	4 $\frac{3}{4}$	14.6%	10% (NH ₄) ₂ SO ₄
4	#15	5	230	250	15	33%	5%
5	#14	5	230	250	4	25%	5%

1. Better recoveries were obtained when (NH₄)₂ SO₄ was added to the ammoniacal solutions.

2. Tests 5, 6 and 7 show that all recoverable cobalt is extracted in the first leach.

3. No cobalt metal was found in the residues from these leaches.

(c) Acid Leaches.

Various acid leaches were tried on different caustic oxidized residues. A summary of these leaches is given in Table 3.

Table 3. Summary of Acid Leaches.

Test No.	Caust. Res Used	Acid strength %	Temp °F	Press. psig	Time	(1) Agit.	Recovery %
1	12	5	180	No O ₂	5	High	69
2	14	8	260	200	3	Low	70
3	2	1	450	No O ₂	4	Low	Trace
4	14	15	210	No O ₂	4	None	70
5	16	5	210	No O ₂	24	High	67

(1) Agitation.

1. These tests show that cobalt is not removed easily from the caustic oxidized residues.

4. Theoretical Considerations.

The reactions occurring, when this cobalt ore is oxidized in aqueous solutions, are undoubtedly very complicated. A great deal of fundamental research will be necessary before such reactions can be completely understood. However, it is possible to utilize thermodynamic data to indicate the type of reactions involved and to predict, in some cases, the end products formed.

The driving force for any chemical reaction can be calculated provided free energy data is available concerning the reactants and possible products of the reaction. Since the free energy of formation of the complex ore is not known, the true driving force for oxidation of the ore cannot be obtained. However, calculations can be made to compare the driving forces of the important elements in the ore; namely, cobalt, iron, arsenic and sulphur. This comparison will be valid if the elements are equally available for oxidation.

Equations for the oxidation of the four elements are given in the appendix. The thermodynamic driving force for each equation has been calculated, and the following results obtained:

<u>Reactant.</u>	<u>Product.</u>	<u>ΔF° cal/mole.</u>
Co	Co(OH) ₂	- 52,200
Co	Co(OH) ₃	- 56,950
Co(OH) ₂	Co(OH) ₃	- 4,640
Fe	Fe(OH) ₂	-58,950
Fe	Fe(OH) ₃	- 81,200
Fe(OH) ₂	Fe(OH) ₃	- 22,250
As	AsO ₄ ⁼	-126,200
S	SO ₄ ⁼	-158,500

A number of general conclusions may be evolved by considering the above free energy values in conjunction with the corresponding equations in the appendix:

1. An indication is given as to the order of oxidation of the elements, i.e.,

Sulphur
Arsenic
Iron
Cobalt

2. The higher oxidized forms of cobalt and iron are more stable than the lower forms and the latter are only present as intermediate products.
3. From the thermodynamic calculations, it appears that greater hydroxide concentration increases the driving force for the oxidation of arsenic and sulphur, but has no effect on that of iron and cobalt.

As will be seen later the caustic concentration affects the solubility of oxygen.

An explanation of the equilibrium in strong caustic solutions can now be presented. Latimer (7) reports that cobaltous hydroxide is soluble in strong caustic solutions, giving a blue solution of the cobaltite ion. Since this hydroxide is an intermediate product in the

(7) Latimer, W.M., "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", Prentice-Hall, New York (1938).

oxidation of cobalt to cobaltic hydroxide, it becomes clear that the cobaltite ion is also an equilibrium product.

An explanation, as to why the oxidation proceeded at a low rate in strong caustic solutions, may be obtained by considering the solubility of oxygen in these solutions. Oxygen solubility at (8) 14.7 psi and 78°F is as follows:

Solubility in water	28.22 ml/litre
" " .5N NaOH	22.9 "
" " 1.0N NaOH	18.7 "
" " 2.0N NaOH	12.2 "

This data has been plotted in Figure 2 at 78°F.

The solubility of slightly soluble gases in aqueous salt solutions is given by:

$$S = S_o \left(A_m + \frac{1}{1 + B_m} \right)$$

where: m = molarity of salt.
 S = gas solubility.
 S_o = gas solubility in water.
 A, B = constants.

By using the above solubility data and solving, it is found that A = - 0.078 and B = 0.356.

(8) "International Critical Tables", Vol.3, pp.271-281.

Then, at zero solubility, $m = 4.65$ molar.

In Figure 2, this value agrees very well with the extrapolated curve at 78°F .

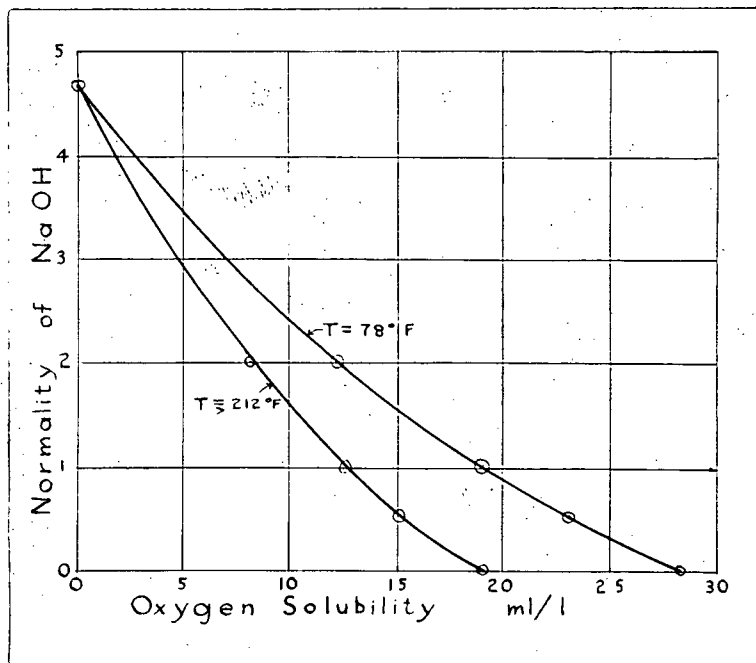


Figure 2. Effect of temperature on the solubility of oxygen in NaOH.

Solubility data for oxygen in water at various temperatures
(9)
is given by Perry. This data is plotted in Figure 3.

Obviously, the solubility of oxygen in water is nearly constant above 100°C . A constant of 1.52 is obtained from Figure 3 as the ratio of oxygen solubilities at 100°C and 25°C . It is then used to replot the data of Figure 2 at 212°F .

(9) Perry, J.R., "Chemical Engineers' Handbook". McGraw-Hill, New York, 1941.

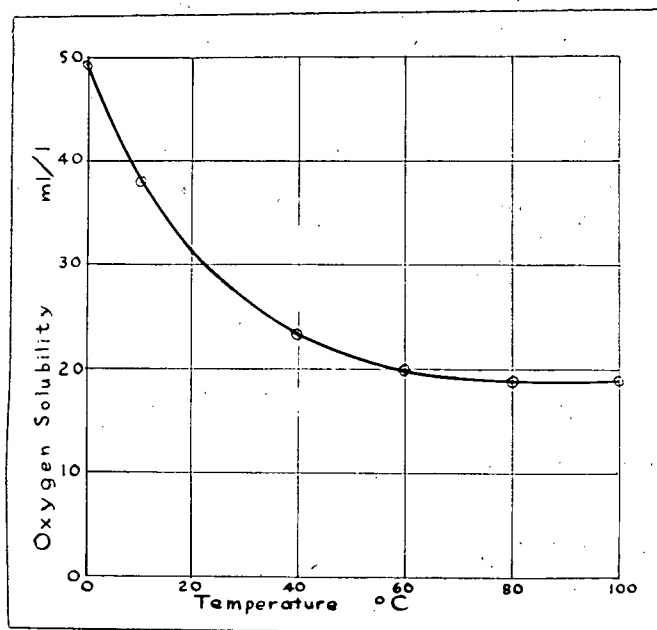
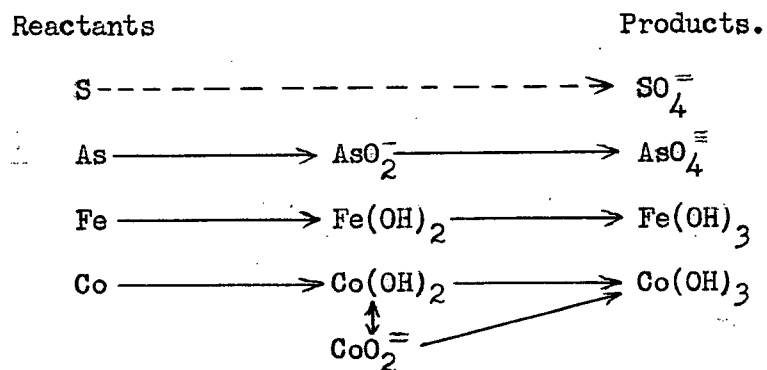


Figure 3. Effect of temperature on the solubility of oxygen in water.

Figure 2 then shows that the solubility of oxygen decreases to approximately zero above a concentration of 4.7 ~~7N~~ caustic.

In summary, the oxidation theory in caustic solution may be shown as follows:



5. Practical Considerations.

(a) Cobalt Recovery.

The results indicated that poor cobalt recoveries could be expected.

(b) Equipment.

1. High pressure oxidation units.

In these units there would be danger of caustic embrittlement.

2. Acid leach units.
3. Filtering equipment.

Since the oxidized residues are difficult to filter, counter-current thickeners would be used.

(c) Reagents.

1. Caustic would be required continually for the initial oxidation. Some of it could be regenerated either by crystallizing sodium arsenate or precipitating calcium arsenate with lime. The sulphate in these leach solutions would be partly eliminated in either of these treatments.
2. Fairly concentrated sulphuric acid leach solutions would be necessary.

PART 5: OXIDATION IN AMMONIACAL SOLUTION.

A. Low Pressure Oxygen Leaches.

1. Equipment.

These leaches were carried out in an 8-litre steel tank, equipped with a mechanical stirrer. A photograph of the apparatus appears on page 22.

2. Procedure.

A standard procedure was adopted in charging the leach tank. The charge consisted of 1500 cc. of concentrated ammonium hydroxide and 30 grams of the material to be leached.

3. Results.

Table 4 - SUMMARY OF LOW PRESSURE LEACHES.

Test No.	Material Leached.	Addition Reagent.	Temp °F.	Time hrs.	% Co. Recovered.
	(1)				
GM-4	C.C.	-	70	8	Trace
19	C.C.	$3\frac{1}{2}\%$ $(\text{NH}_4)_2\text{CO}_3$	70	$4\frac{1}{2}$	Trace
22	C.C.	7% $(\text{NH}_4)_2\text{CO}_3$	115	4	Trace
18	#2 Calcine	-	70	$4\frac{1}{2}$	Trace
21	#1 Calcine	-	70	8	Trace
	(2)				
17	C.O.R.	-	70	5	Trace

(1) composite concentrate.

(2) caustic Oxidized Residue.



Figure 4. Low pressure leach unit.

1. No cobalt was extracted from the composite concentrate, calcines, or caustic oxidized residue.
2. No evidence of oxidation was noted.

B. High Pressure Oxidation in Ammoniacal Solution.

1. Equipment and Procedure.

The same autoclave was used as previously described in the caustic treatment and the same general procedure was followed.

2. Results.

(a) High Pressure Oxidation.

A summary of all the high pressure ammonium hydroxide leaches is presented in Table 5.

1. Conditions of treatment were varied widely in tests 1 to 15 in an attempt to increase the extraction of cobalt. The maximum recovery, however, was 35%.
2. The results indicated that the soluble cobalt ammonium^(on) was an equilibrium product.
3. In tests 16 and 17 the cobalt was completely removed from solution and the residue appeared to be some form of insoluble arsenate.
4. A decrease in ammonium hydroxide concentration reduced the time and pressure necessary for complete oxidation.
5. The rate of oxidation was materially increased by

TABLE 5 - SUMMARY OF HIGH PRESSURE AMMONIA OXIDATIONS

No.	Test Mater- No.	% Solids	NH ₄ OH Conc. %	Temp °F	Total Time Press. hrs. psig	%C ₆ in Sol'n	% Change in wt. of Residue	Remarks.
	(1)							(2)
1	24 C.C.	20	28	220	200	3	15 +13.6	P.O.
2	27 C.C.	20	28	220	200	8	4 +18	P.O.
3	29 GM-24	20	28	220	200	2½	Nil + 4	P.O.
4	25 C.C.	10	28	220	200	3	22 + 9.6 10%(NH ₄) ₂ CO ₃	P.O.
5	41 C.C.	20	28	250	250	1¾	30 - 3	P.O.
6	34 C.C.	10	28	350	475	2	Nil - 10%CaO	(3) N.O.
7	36 C.C.	10	28	250	475	2	Nil - 10%CaO	N.O.
8	69 GM-200	20	28	220	200	2	Nil - 5	N.O.
9	70 -200	20	28	220	200	5	Nil - 5	N.O.
10	73 200	20	28	265	300	2½	4 - 2	P.O.
11	72 200	20	7	265	300	2½	35 - 14	P.O.
12	74 200	20	3	265	300	2½	25 - 3	P.O.
13	75 200	20	3	265	300	4	Nil - 1	P.O.
14	76 200	13	3	265	300	2¼	Nil +12.5 Grd.	(4) C.O.
15	90 200	17	3	350	350	3	4 + 3	P.O.
16	95 200	13	3	380	380	15	Nil +17.5 Grd.	C.O.
17	106 200	20	3	380	380	15	Nil +22.7	C.O.

(1) Composite concentrate.

(2) Partly oxidized.

(3) No oxidation.

(4) Completely oxidized.

grinding the ore in a pebble mill and transferring it to the autoclave without filtering and drying.

6. The reaction was stopped completely when lime was added to the charge.

(b) Acid Leaches of Ammonia Oxidized Residues.

The oxidized residues from test nos. 16 and 17 in Table 5 were leached in sulphuric acid to determine the cobalt extraction. These leaches were made in open beakers with intermittent stirring. Table 6 shows the results of these leaches.

TABLE 6 - SUMMARY OF ACID LEACHES ON AMMONIA OXIDIZED RESIDUES.

No.	Oxidized Residue No.	Acid Strength %	Time hrs	Recovery %	Temp. °F.
1	# 16	60	5 (1)	29	170
2	# 16	25	8	99	170
3	# 17	25	5	94	170
4	# 17	13	5	94	170
5	# 16	5	4	79	180

(1) 8 hours heating and 30 hours before filtering.

1. These results indicated a definite possibility of extracting nearly all the cobalt from the ammonia oxidized residues.

A composite residue was then produced by oxidizing several batches of GM-200 in dilute ammoniacal solutions. This residue was called GM-400 and had the following analysis:

Co	Fe	As	S
4.8%	18.0%	30.0%	0.23%

This residue was used as a head sample for the acid leaches in Table 7.

TABLE 7 - ACID LEACHES OF GM-400

No.	% Acid	% Solids	Temp. °F.	Time hrs	Type of Leach.	% Co. Rec.	% Fe in Sol'n	% As in Sol'n	Res. Wt % of Heads.
401	25	10	70	24	(1) B.L.	69	84	90	15
402	13	10	70	24	B.L.	56	84	82	24
403	5	10	70	24	B.L.	19.2	73	67	41
409	5	2	70	24	B.L.	20.8	83	77	27
411	5	2	200	4½	No Agit.	83	72	-	19
412	5	10	200	15	(2) B.L.S.	95	25	31.8	68

Winchester.

(1) B.L. Bottle leach.

(2) B.L.S. Beaker leach with stirring.

1. In addition to the tests shown in Table 7 two other leaches were made with GM-400, both of which were designed to eliminate arsenic from the acid leach solution. These tests were as follows:

(i) A 2.5:1 mixture of GM-400 and ferric sulphate were leached in 5% sulphuric acid at 200°F for 24 hours. The As in solution was reduced to 5.0% but the Co recovery dropped to 75%

(ii) GM-400 was leached with 1 N NaOH to eliminate arsenic and the residue leached in 5% sulphuric acid for 6 hours. Only 17% of the cobalt was extracted and 6% of the arsenic was left in solution.

2. In Figure 5, the effect of sulphuric acid concentration on the recovery of cobalt is indicated for cold acid leaching of GM-400.

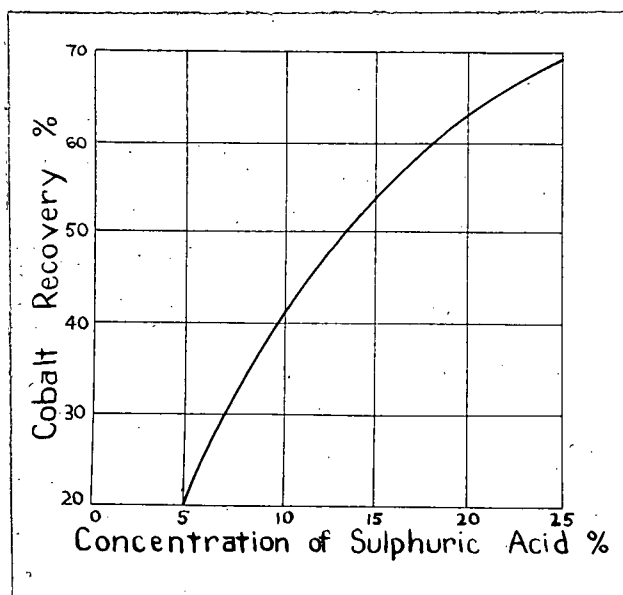


Figure 5. Effect of Sulphuric Acid concentration on Recovery of Cobalt. (Cold acid leach of GM-400)

3. In test 412, 95% cobalt extraction was obtained. The iron and arsenic in the residue were combined as an iron acid arsenate, having the formula $2 \text{Fe}_2(\text{HAsO}_4)_3 \cdot 9\text{H}_2\text{O}$. Apparently the final PH of the solution is critical. If it is low iron arsenate will not precipitate, and if it is high cobalt arsenate will precipitate.

(c) Solution Purification.

The purification of cobalt solutions containing iron and arsenic is discussed in the publication, "Electro-winning of Cobalt from Cobaltite Concentrates"⁽¹⁰⁾. To precipitate ferric arsenate a minimum of 1.5 equivalents of ferric iron must be present per equivalent of arsenic; smaller amounts of ferric iron cause cobalt arsenate to precipitate.

The solution from test 412 was subjected to precipitation experiments using lime, sodium carbonate and sodium hydroxide as precipitating materials. Since the iron to arsenic equivalence ratio in the solution was only 1.05:1, the arsenic could not be entirely eliminated without precipitating some cobalt. This result, having proved the purification step to be inadequate, suggested the use of two alternative processes. In the first modification, iron would be added at an early stage of the process, preferably as iron sulphide, before the

- (10) Shelton, F.K., Stahl, J.C., Churchward, R.E., "Electrowinning of Cobalt from Cobaltite Concentrates", U.S. Bur. Mines Rept. Investigations, 4172, (1948).

ammonia oxidation. The second alternative would be to leach the ammonia oxidized residue with caustic and follow with a strong acid leach.

As a matter of interest, the approximate order of the precipitations, with rising PH, is given in Table 8.

TABLE 8 - APPROXIMATE ORDER OF PRECIPITATION FROM ACID SOLUTION.

PH Range.	Type of Precipitate.	Type of Solution.
0.5 to 0.75	$\text{Co}_3(\text{asO}_4)_2 \cdot 1.5\text{FeAsO}_4 \cdot 10\text{H}_3\text{AsO}_4$	High As and Fe.
1.2 to .18	FeAsO_4	All types containing Fe & AsO_4
2.5 to 3.5	Copper Arsenate	When Cu is present
2.9 to 3.5	$\text{Fe}(\text{OH})_3$	If excess Fe is present
3.2 to 5.0	Cobalt Arsenate	If insufficient Fe is present
About 3.8	$\text{Al}(\text{OH})_3$	Solution containing Al.
4.2 to 5.2	Complex copper carbonates	Solutions with residual Cu.
About 5.2	Cd, Zn carbonates	
5.1 to 6.5	Calcium carbonate	If insufficient Fe is present.

3. Theoretical Considerations.

The equations for the oxidation of iron, cobalt, and sulphur in ammoniacal solutions are given in the appendix. Driving forces, based on standard electrode potentials, have no significance in these solutions and

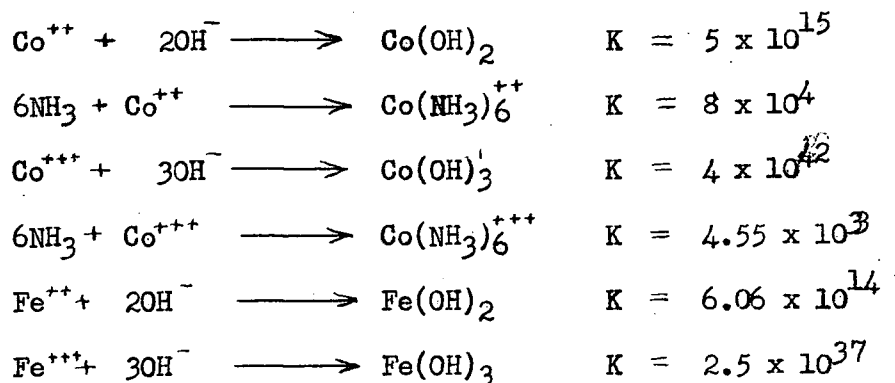
will not be presented here. However, the stabilities of the various products in different ammoniacal solutions may be used to indicate which products are most likely to be formed.

The stabilities will be determined in solutions containing 28, 3, and 3×10^{-7} weight percent ammonia. The concentrations of ammonia and hydroxal ion are as follows:

Weight % NH_3	Concentration NH_3 moles/litre	Concentration OH^- moles/litre
28	16.5	1.75×10^{-2}
3	1.76	5.71×10^{-3}
3×10^{-7}	1.76×10^{-7}	1.81×10^{-6}

(11)

The following equilibrium constants are given by Latimer.



This data is then used to calculate the stability of various products in the different ammonia solutions. The results are given in Table 9. The effect of arsenic on these values will be considered separately.

(11) Latimer, "Oxidation Potentials", Prentice-Hall, New York (1938).

TABLE 9 - STABILITIES OF VARIOUS COMPOUNDS IN AMMONIA SOLUTIONS.

	ΔF°	ΔF		
Conc. NH_3	1	16.5	1.76	1.76×10^{-7}
Conc. OH^-	1	1.75×10^{-2}	5.71×10^{-3}	1.81×10^{-6}
$\text{Co}(\text{OH})_2$	- 21,400	- 16, 600	- 15, 300	- 5,750
$\text{Co}(\text{NH}_3)_6^{++}$	- 6,700	- 16,600	- 8,700	+ ———
$\text{Co}(\text{OH})_3$	- 58,100	- 50,900	- 49,000	- 34,600
$\text{Co}(\text{NH}_3)_6^{+++}$	- 46, 000	- 55,800	- 47,900	+ ———
$\text{Fe}(\text{OH})_2$	- 20,200	- 15,350	- 14,000	- 4, 500
$\text{Fe}(\text{OH})_3$	- 51,000	- 43,800	- 41,900	-27,400

Note: The metal ion and complex ion concentrations are assumed to be one molar.

The significance of the stability values in Table 9, as applied to the oxidation of an ore containing no arsenic may be outlined as follows:

1. The higher oxidized form of each element is the more stable.
2. In concentrated solutions of ammonia the cobalt-ammonium complex is more stable than cobaltic hydroxide but in dilute solutions the reverse is true. If the concentration of the complex is decreased its stability is increased.

3. An equilibrium between cobaltic hydroxide and the cobaltic complex will exist, and be dependent on the ammonia concentration.

When arsenic is present in the ore in appreciable amounts the oxidation products become very complex. Cobalt and iron arsenates are undoubtedly formed but their stabilities cannot be evaluated because thermodynamic data is lacking. Since the appearance of the residue is changed considerably by slight changes in the final PH of the solution, it is likely that a wide variety of arsenate compounds are formed, containing different amounts of water and ammonia. Three cobalt aminorthoarsenates, reported by Mellor ⁽¹²⁾, have the general composition $\text{Co}_3 (\text{AsO}_4)_2 \cdot n \text{NH}_3 \cdot (8-n)\text{H}_2\text{O}$, where n is 1, 2 or 3. The form of the arsenate depends on the free ammonia present. These arsenates are quite insoluble in ammonium hydroxide but can be dissolved readily in acids. Iron may be present in the residue as the ferrous or ferric orthoarsenate, $(\text{Fe}_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}, \text{FeAsO}_4 \cdot 2\text{H}_2\text{O})$, which are only slightly soluble in ammonium hydroxide.

Since these arsenates are thought to be the final product in the ammonia oxidized residue, they must be more stable, in dilute ammonia solutions, than either the hydroxide or the amines. In concentrated ammonia solutions, however, an equilibrium may exist between cobalt

(12) Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 9, Longmans Green & Co., 1928.

in solution as the amine and in the residue as the arsenate. This reasoning explains why complete oxidation could be carried out more easily in dilute than in concentrated ammonia solutions.

An outline of the suggested reactions in the oxidation of the ore in ammoniacal solution is shown in Figure 6.

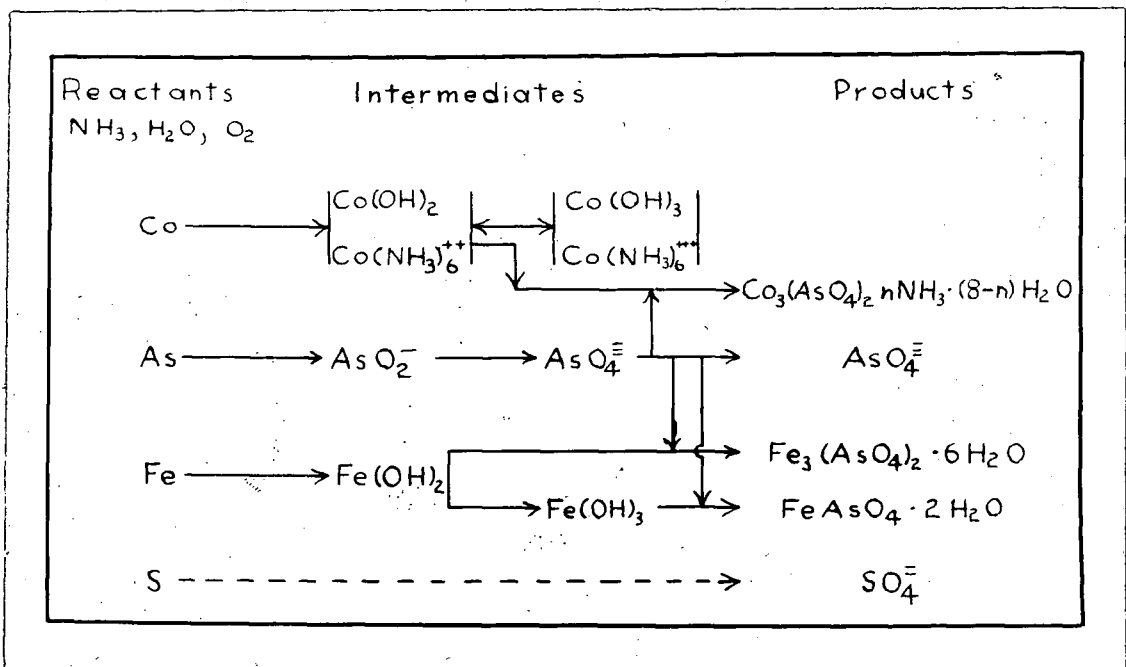


Figure 6. Outline of oxidation in ammoniacal solution.

4. Practical Considerations.

A practical process for treating Taylor Gem ore to recover cobalt may be outlined as follows:

- (1) Oxidize the ore in dilute ammoniacal solution.

- (2) Leach the arsenate residue in hot, dilute sulphuric acid adjusting the final PH so that maximum elimination of iron and arsenic from the solution is accomplished without loss of cobalt.
- (3) Filter the above solution and make a final PH adjustment with NaOH or Na_2CO_3 to eliminate most of the arsenic and iron. Should cobalt be precipitated during this step the residue can be leached with NaOH to remove arsenic, and the iron and cobalt can be returned to the acid leach.
- (4) Take one of two corrective measures if the iron to arsenic ratio is not great enough for effective removal of arsenic.
 - (a) Add pyrite in the oxidation step to increase the iron to arsenic ratio.
 - (b) Leach the oxidized residue with caustic and treat this residue with fairly concentrated sulphuric acid.
- (5) Recover the cobalt from solution in marketable form. The best method for so doing has not been considered but one of two methods could be used.
 - (a) Electrolytic.
 - (b) Precipitation of cobaltic hydroxide in neutral solutions.
- (6) Cyanide the residue from the acid leach to recover the gold content of the ore.

Cobalt Recovery.

Between 90 and 100% cobalt recovery can be obtained by using the method of treatment outlined. Larger scale research will be required to get a precise percentage of recovery from ore to finished product.

Reagents.

Enough ammonia should be used in the oxidation step to ensure a PH of 8 or 9 in the resulting solution. The split between ammonia in solution and in residue was not determined but what is in solution may be recovered by heating and liming. Ammonium sulphate may also be recovered from the oxidation solution but it would however, be contaminated with arsenic.

If caustic were used in leaching the oxidized residue, it could be regenerated with lime to produce a marketable product, $\text{Ca}_3 (\text{AsO}_4)_2$.

Sulphuric acid, in sufficient quantity, would be necessary in the acid leach solution at all times to prevent cobalt arsenate from precipitating. The acid solution, after purification and cobalt precipitation, may be either rejected or evaporated to recover sodium and ammonium sulphate.

Equipment.

Although optimum conditions of ore grinding and oxidation

were not ascertained, it appears likely that pressure equipment capable of operating between 300 and 400 psig would be necessary.

Corrosion or embrittlement of equipment was not severe and stainless steel would offer the least difficulty in this respect.

PART 6: OXIDATION IN WATER SOLUTION.

1. Equipment.

The autoclave used in this series of tests differed from the one previously employed only in materials entering into its construction. High pressure pipe and a heavy flange and end plate would permit operations at up to 900 psig. Because of acid solutions produced during the oxidation of the ore, an acid resistant coating was necessary to protect the autoclave from corrosion. No temperatures above 400°F could be used without cracking this coating. A photograph of the apparatus is shown in Figure 7.

2. Procedure.

The charge to the autoclave consisted of 75 grams of GM-200, or GM-200 plus Britannia pyrite, and 600 c.c. of water giving a solid to liquid ratio of 1 to 12.5. With this exception procedure was unchanged from that used for oxidation in caustic.

3. Results.

The purpose of the oxidations in water solutions was to produce an acid solution of sufficient strength so that iron and arsenic would be precipitated as iron arsenate while cobalt remained in solution. Britannia pyrite was added to the charge in some cases to supply an excess of iron and to produce a more acid solution. This pyrite has



Figure 7. Autoclave for Oxidation in Water Solution.

the following composition:

Fe - 44.8%

S - 36.7%

Insol - 9.8%

In table 10, the essential details of tests made in water solutions are shown. Unless a modification is indicated in the "Addition" column, the charge in any test consisted of 75 grams of GM-200 plus 600 c.c. of water.

1. Tests 1 to 3 indicate that at fairly high temperatures and pressures about 80% cobalt extraction was possible in water solutions. The solutions are free of Fe but contain 30% of the original arsenic.
2. On the addition of pyrite, nearly all the As is eliminated from solution and cobalt extraction is increased to 85%.
3. Tests 5 to 7 show that the critical temperature for oxidation of the ore with pyrite lies between 210 and 230°F.
4. Oxidation of cobalt is aided appreciably by the pressure of pyrite but not by sulphuric acid. This suggests that the presence of pyrite in the charge aids the oxidation of cobalt, not by increasing the acidity of the solution, but by lowering the potential barrier for that oxidation.
5. In test 10, arsenic and iron contamination is bad because of the high acidity of the solution.

(13)

TABLE 10 - SUMMARY OF OXIDATION IN WATER TESTS.

No.	Test No.	Addition	Temp. °F	Press psig	Time hrs.	In Solution.		
						% Fe	% As	% Co
1	150	-	300	200	4	Nil	31.6	70.0
2	151	-	300	200	15	Nil	27.6	83.0
3	152	-	350	380	3	1.2	29.8	81.7
4	153	41.4 % Py	250	180	15	-	Tr.	85.6
5	155	41.4 % Py	212	50	24	-	Tr.	84.5
6.	156	41.4 % Py	220	35	15	-	19.7	78.0
7	158	47.5 % Py	225	40	15	Nil	12.0	53.3
8	159	41.4% Py	225	40	15	Nil	15.9	53.4
9	160	-	225	40	15	Nil	10.7	12.1
10	161	6% H ₂ SO ₄	225	40	15	51	42.7	27.5
11	169	40 % Py	250	60	1	-	-	19.7
12	167	40 % Py	250	60	2	-	8.7	36.7
13	165	40 % Py	250	60	4	-	-	40.0
14	164	40 % Py	250	60	6½	-	-	49.8
15	168	40 % Py	250	60	11	-	13.0	75.8
16	166	40 % Py	250	60	17	-	-	67.8
17	163	40 % Py	250	60	24	4.7	3.5	87.0

(13) In column 3 an addition of 41.4% Py indicates that a charge consisted of 44 grams GM-200 plus 31 grams of Brittania pyrite. Percentages of product in solution are in terms of the amount present in the ore before oxidation.

6. When the temperature is low, insufficient iron is oxidized to precipitate the arsenic.

7. From tests 11 to 17 the rate of oxidation of cobalt and sulphur was obtained and is shown in Figure 8.

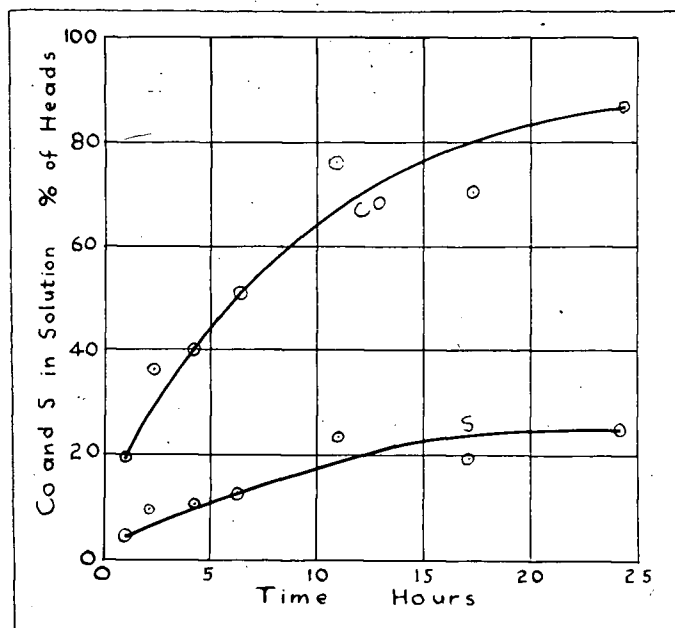


Figure 8 Rate of oxidation of cobalt and sulphur in water.
(Temperature 250°F, pressure 60 psig).

4. Theoretical Considerations.

Equations for the oxidation of Fe, Co, As and S in acid solution are given in the appendix. The driving forces for the oxidation of these elements have been calculated in one molar acid and neutral solutions, as shown in Table 11.

TABLE 11 - DRIVING FORCES IN ACID AND NEUTRAL SOLUTIONS.

Element	Product.	ΔF° Cal/mole	ΔF at $10^{-7}(H^+)$ cal/mole
Iron	Fe^{++}	- 77,000	- 57,900
	Fe^{+++}	- 87,600	-59,000
Cobalt	Co^{++}	-69,400	- 50,400
	Co^{+++}	- 55,400	- 26,800
Sulphur	$SO_4^{=}$	-118,000	-138,200
Arsenic	H_3AsO_4	- 98,000	-127,600

In addition, the following ionic equilibria would exist:

$$\frac{(Fe^{+++})}{(Fe^{++})(H^+)} = 3.16 \times 10^8$$

$$\frac{(Co^{+++})}{(Co^{++})(H^+)} = 5.6 \times 10^{-32}$$

In a hypothetical oxidation in which no compounds are formed the following observations can be made from the above calculations:

1. The order of oxidation of the elements in acid and neutral solutions is as follows:

sulphur
arsenic
iron
cobalt.

2. The driving forces for the oxidation of Fe and Co are decreased and those for S and As increased as the hydrogen

ion concentration is lowered.

3. In one molar acid solutions the stable form of iron is the ferric ion and that of cobalt the cobaltous ion. As the hydrogen ion is decreased ferric ion becomes less stable and cobaltous ion more stable.

If compound formation is considered the above observations become invalid. When no arsenic is present, the higher oxidized forms of iron and cobalt hydrolyze in neutral solution, and if arsenic is present insoluble arsenates are formed.

A white residue, probably composed of iron, cobalt, and calcium arsenates, was formed in the oxidation of the arsenide ore in water. The exact structure of these compounds is not known but a clue to the type of iron arsenate present was obtained in a simple test. By evaporating an acid solution containing iron, arsenic, and cobalt a white precipitate was obtained which was dried and analyzed. The calculated formula of this compound, $2\text{Fe}_2(\text{As O}_4)_3 \cdot 9\text{H}_2\text{O}$, agreed closely to the Mellor formula for a white compound, $2\text{Fe}_2(\text{H As O}_4)_3 \cdot 9\text{H}_2\text{O}$. Numerous other arsenate compounds could be present in the white residue from the ore oxidation but none were identified.

5. Practical Considerations.

Although the number of tests made in water solutions was limited, it is apparent, from these, that at least 85% of the cobalt can be leached

from Taylor Gem ore. While this recovery would not ordinarily be high enough to warrant practical consideration, it definitely indicates good potentialities in this case because of the low cost of reagents. In addition, a higher overall recovery could possibly be obtained by a simple acid leach of the oxidized residue. The gold content of the ore should be easily recoverable by cyanidation of the residue.

Equipment.

The main problem to be overcome in a process involving acid solutions under oxygen pressure is that of corrosion of equipment. Even though the results indicate that low temperatures and pressures (250°F and 60 psig) could be used, the corrosion rate on ordinary steel containers would be high. Stainless steel reactors would prove more satisfactory but would still, undoubtedly require some protection. Cathodic protection measures offer distinct possibilities in this regard. Various types of organic protective coatings would also warrant investigation as some might prove feasible.

PART 7: CONCLUSIONS.

A multitude of tests were performed on a cobalt-arsenide ore from the Taylor Gem Mine in an effort to recover cobalt by oxidation in aqueous solutions under oxygen pressure. These experiments covered a wide range and, in some cases, were not complete enough to furnish all the facts regarding particular phases of the investigation. Although uranium was present in the GM-200 sample used in most of the tests, the quantity was too minute to permit the tracing of its eventual disposition. As for cobalt recovery, however, the results were sufficiently conclusive to indicate the advantages and disadvantages of several methods of treatment.

The three principle methods of treatment upon which examinations were made, together with the known advantages and disadvantages of each, will be outlined below. For conclusions concerning the theoretical treatment of the investigation the reader is referred to the sub-headings, "Theoretical Considerations", to be found under the main headings for each type of oxidation.

In the first process, oxidation of the ore in a dilute caustic solution removes all the sulphur and most of the arsenic. The resulting residue appears to consist of iron and cobalt oxides or hydroxides which may then be leached in sulphuric acid. This process has the advantage of obtaining very good arsenic elimination provided

the caustic concentration is about six normal. However, several disadvantages may be noted:

- (a) Fairly strong, hot acid is necessary to dissolve the residue.
- (b) The acid leach solution is badly contaminated with iron.
- (c) Filtration is slow.
- (d) The reacting vessel is subject to caustic embrittlement.

The second method of treatment, in which the cobalt ore is oxidized in ammonium hydroxide solution, yields a totally different type of residue to that of the first method. This residue, probably consisting of cobalt aminoarsenates and iron arsenates, is also leached in sulphuric acid. Advantages of this method were found to be as follows:

- (a) A residue is produced from which 95% of the cobalt can be leached with warm, 5% sulphuric acid.
- (b) Corrosion of the reactor is slight.
- (c) All residues are easily filterable and have high settling rates.

Certain disadvantages were also made apparent by the investigations, these being:

- (a) At the temperatures required for oxidation the ammonia partial pressure is high thereby making the total pressure necessarily high.
- (b) Arsenic cannot be completely precipitated during the

purification step, without cobalt being precipitated, unless an external supply of iron is introduced.

In the third method of treatment, oxidation of the ore is carried out in water, with, or without, the addition of pyrite to the charge. As advantages of this method the following factors are indicated:

- (a) A solution containing 90% of the cobalt and only small amounts of iron and arsenic is obtained when sufficient iron in the form of pyrite is added.
- (b) Low temperatures and pressures can be used in the oxidation.
- (c) Cost of reagents is very low.
- (d) Filtration and settling rates are quite fast.

The main disadvantage of the process is the severe corrosion of equipment which takes place.

Recovery of cobalt by oxidation in either ammonium hydroxide or water solutions appears quite feasible. The water process, in particular, would be most satisfactory if the corrosion problem can be eliminated.

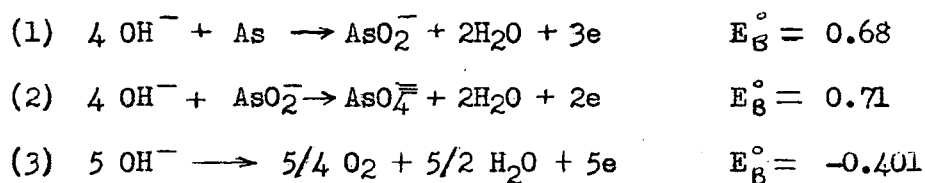
PART 8: APPENDIX.

1. Calculations of driving forces in basic solutions.

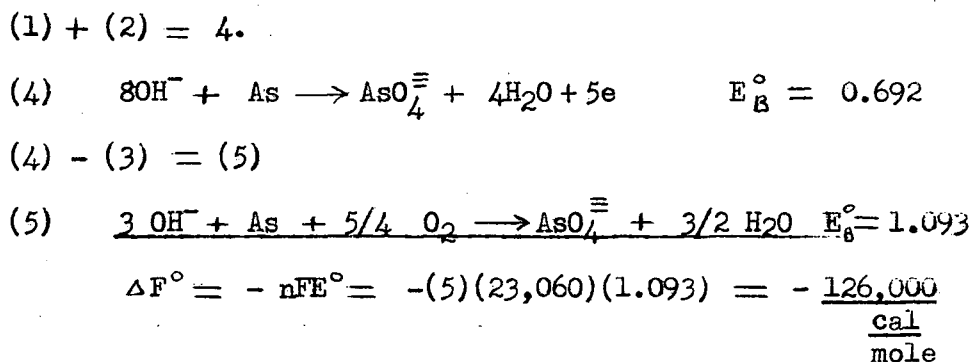
All the equations used are from Latimer.

Arsenic.

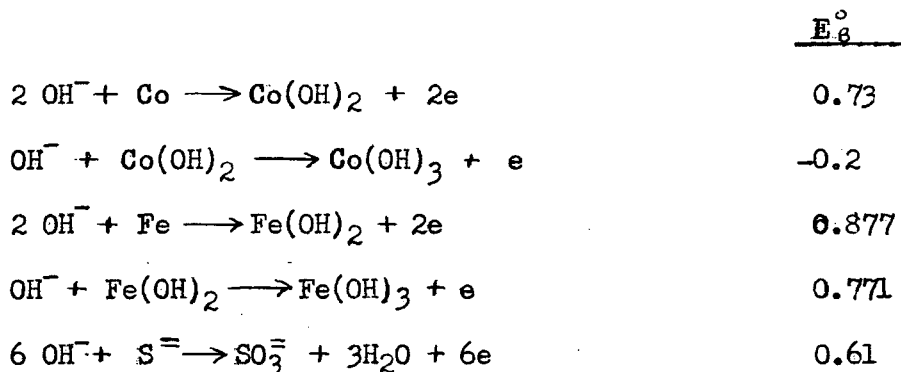
Equations used:



Then



By similar methods the equations for the oxidation of cobalt, iron and sulphur have been calculated from the following data:



	<u>E^o_a</u>
$S^{=}\longrightarrow S + 2e$	0.508
$2OH^{-} + SO_3^{=}\longrightarrow SO_4^{=} + H_2O + 2e$	0.90
$2OH^{-}\longrightarrow 1/2 O_2 + H_2O + 2e$	-0.401

The results are as follows:

	<u>ΔF^o cal/mole</u>
$Co + 1/2 O_2 + H_2O \longrightarrow Co(OH)_2$	-52,200
$Co + 3/4 O_2 + 3/2 H_2O \longrightarrow Co(OH)_3$	-56,950
$Fe + 1/2 O_2 + H_2O \longrightarrow Fe(OH)_2$	-58,950
$Fe + 3/4 O_2 + 3/2 H_2O \longrightarrow Fe(OH)_3$	-81,200
$2OH^{-} + S + 3/2 O_2 \longrightarrow SO_4^{=} + H_2O$	-158,500

2. Calculations of driving forces in ammonia solutions.

The following equations are used:

	<u>E^o_a</u>
$6NH_3 (aq) + Co \longrightarrow Co(NH_3)_6^{++} + 2e$	0.422
$Co (NH_3)_6^{++} \longrightarrow Co(NH_3)_6^{+++} + e$	-0.1
$2OH^{-}\longrightarrow 1/2 O_2 + H_2O + 2e$	-0.401

The results are as follows:

	<u>ΔF^o</u>
$6NH_3 (aq) + Co + 1/2 O_2 + H_2O \longrightarrow Co(NH_3)_6^{++} + 2OH^{-}$	-28,000
$6NH_3 (aq) + Co + 3/4 O_2 + 3/2 H_2O \longrightarrow Co(NH_3)_6^{+++} + 3OH^{-}$	-44,950

3. Calculations of driving forces in acid solutions.

The following equations are used:

	<u>E°</u>
$\text{Fe} \longrightarrow \text{Fe}^{++} + 2\text{e}$	0.441
$\text{Fe} \longrightarrow \text{Fe}^{+++} + \text{e}$	-0.771
$\text{Co} \longrightarrow \text{Co}^{++} + 2\text{e}$	0.277
$\text{Co}^{++} \longrightarrow \text{Co}^{+++} + \text{e}$	-1.84
$2\text{H}_2\text{O} + \text{As} \longrightarrow \text{H}_3\text{AsO}_2 (\text{aq}) + 3\text{H}^+ + 3\text{e}$	-0.2475
$2\text{H}_2\text{O} + \text{HAsO}_2 \longrightarrow \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}$	-0.559
$3\text{H}_2\text{O} + \text{S} \longrightarrow \text{H}_2\text{SO}_3 + 4\text{H}^+ + 4\text{e}$	-0.45
$\text{H}_2\text{O} + \text{H}_2\text{SO}_3 \longrightarrow \text{SO}_4^{--} + 4\text{H}^+ + 2\text{e}$	-0.20
$2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}$	-1.229

The results are as follows:

	<u>ΔF°</u>
$\text{Fe} + 1/2 \text{O}_2 + 2\text{H}^+ \longrightarrow \text{Fe}^{++} + \text{H}_2\text{O}$	-77,000
$\text{Fe} + 3/4 \text{O}_2 + 3\text{H}^+ \longrightarrow \text{Fe}^{+++} + 3/2 \text{H}_2\text{O}$	-87,600
$\text{Co} + 1/2 \text{O}_2 + 2\text{H}^+ \longrightarrow \text{Co}^{++} + \text{H}_2\text{O}$	-69,400
$\text{Co} + 3/4 \text{O}_2 + 3\text{H}^+ \longrightarrow \text{Co}^{+++} + \text{H}_2\text{O}$	-55,400
$\text{As} + 5/4 \text{O}_2 + 3/2 \text{H}_2\text{O} \longrightarrow \text{H}_3\text{AsO}_4$	-98,950
$\text{S} + 3/2 \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{--} + 2\text{H}^+$	-118,000

In the calculation of the above free energy values it has been assumed that each substance is in its standard state, that is, one molar solutions for the ions and one atmosphere pressure

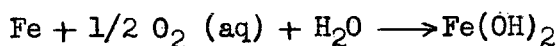
for the oxygen. The following reasons are given for leaving them in this form:

- (1) Since the concentrations are continually changing during the oxidation of the ore, there is no advantage in choosing any other concentration.
- (2) The values may be directly compared to indicate which oxidation has the greatest driving force.
- (3) The correction for oxygen solubility and pressure is not large as will be shown in the following section.

4. Effect of oxygen pressure and solubility on driving force.

The correct form of all the equations which are used in this report should contain oxygen as O_2 (aq) instead of O_2 (g).

Consider the reaction:

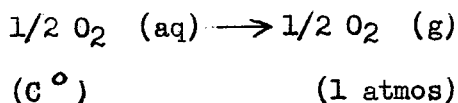


An equation will be derived to calculate the effect of oxygen solubility and pressure on this reaction.

$$(1) \quad \Delta F = \Delta F^\circ + RT \ln \frac{1}{(C_{O_2})^{1/2}}$$

$$(2) \quad \Delta F^\circ = F^\circ_{Fe(OH)_2} - F^\circ_{H_2O} - 1/2 F^\circ_{O_2 (aq)}.$$

To obtain $1/2 F^\circ_{O_2 (aq)}$ consider the following reaction:



Where C° is the concentration of O_2 in water at the standard state of 1 atmosphere.

$$\begin{aligned}\Delta F^\circ &= -RT \ln(P_{O_2}/C^\circ_{O_2})^{\frac{1}{2}} \\ &= -RT \ln(1/C^\circ_{O_2})^{\frac{1}{2}}\end{aligned}$$

Also

$$\begin{aligned}\Delta F^\circ &= 1/2 F^\circ_{O_2} (g) (1 \text{ atm}) - 1/2 F^\circ_{O_2} (aq) (C^\circ) \\ (3) \therefore -1/2 F^\circ_{O_2} (aq) &= -1/2 F^\circ_{O_2} (g) (1 \text{ atm}) \\ &\quad - RT \ln 1/(C^\circ_{O_2})^{\frac{1}{2}}\end{aligned}$$

where $F^\circ_{O_2} (g) (1 \text{ atm}) = 0$

substitution of (3) into (2) gives:

$$\Delta F^\circ = F^\circ_{Fe(OH)_2} - F^\circ_{H_2O} - RT \ln 1/(C^\circ_{O_2})^{\frac{1}{2}}$$

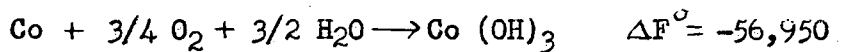
and substitution of (4) into (1)

$$\begin{aligned}\Delta F &= F^\circ_{Fe(OH)_2} - F^\circ_{H_2O} - RT \ln 1/(C^\circ_{O_2})^{\frac{1}{2}} + RT \ln 1/(C_{O_2})^{\frac{1}{2}} \\ \therefore \Delta F &= \Delta F^\circ + 1/2 RT \ln \frac{C^\circ_{O_2}}{C_{O_2}}\end{aligned}$$

The ratio $C^\circ_{O_2}/C_{O_2}$ reduces to $1/P_{O_2}$ as long as Henry's law is followed and the term C_{O_2} takes into account the solubility of oxygen in the particular medium in which it is applied. In strong caustic solutions, for example, the solubility of oxygen approaches zero and C_{O_2} becomes very small. The second term in above expression, therefore, attains a large positive value which cancels the negative driving force of ΔF° .

In dilute caustic solutions, the solubility of oxygen has a very minor effect on the driving force for the reaction.

For example in the reaction:



$$\Delta F = \Delta F^\circ + RT \ln C^\circ/C$$

In 2N caustic O_2 solubility = 12.2 ml/l.

and in water O_2 solubility = 28.22 ml/l

Calculating ΔF at 9 atmospheres O_2 pressure gives:

$$\Delta F = \Delta F^\circ + (1364) \frac{3}{4} \log \frac{28.22}{12.2 \times 9}$$

$$= -56,950 + (1364) \left(\frac{3}{4}\right) (.59)$$

$$\Delta F = -56,950 + 560 = \underline{-56,390.}$$

The effect of oxygen concentration on the driving force is very small. The rate of the reaction, however, will be greatly reduced as the oxygen solubility decreases.

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