Metallurgy for the Retreatment of Cobalt Residue

A Thesis

Submitted to the Faculty of the College
of Engineering in Candidacy for the
Degree of Metallurgical Engineer

(Department of Metallurgy
Mackay School of Mines
University of Nevada)

by

Angus Y. Bethune

Kellogg Idaho

1938.

Foreword.

This thesis is based on a metallurgical report submitted by the author to Mr. W. G. Woolf, Superintendent of the Electrolytic Zinc Plant of the Sullivan Mining Company at Kellogg, Idaho. In it are given the experimental data and the original research performed during the period from June to December 1937.

In the ordinary course of zinc hydrometallurgy the zinc sulphate solutions must be purified of copper, cadmium and cobalt before being subjected to electrolysis. The resulting precipitate containing these impurities is known as Purification Residue. This precipitate is worked to extract the copper and cadmium therefrom, and to produce zinc sulphate solution of sufficient purity to allow it being returned to the main solution circuit. The copper is recovered as cement copper and is shipped to a smelter, while the cadmium is produced as high-grade (99.95%) electrolytic metal. It is in the purification of the zinc sulphate solutions that a residue similar in character, but different in grade than the first named purification residue, is made. Because it is the result of purifying mainly for cobalt (the bulk of the copper and cadmium having already been removed) it is called locally, "Cobalt Residue".

To date this residue has been stored awaiting a time when economic conditions would warrant a retreatment campaign. The recovery of the amount of zinc, cadmium and cobalt tied-up in the residue, although it is considerable, is not imperative at the present time. However the problem will become more acute as the storage pile continues to grow and is one which must eventaally be met. In anticipation of that day when the amount stored is worthy of recovery and favorable conditions prevail this investigation of the reworking possibilities of the Cobalt Residue was undertaken.

The small quantity of residue which is periodically available does not permit continuous metallurgy and precludes the construction of a plant requiring large capital outlay. The problem must be met by treating large batches of stored cobalt residue in short time intervals in order to keep labor costs within reasonable bounds. Unless some other residue, capable of being reworked, were purchased, the plant would remain idle for more time than it was used, and consequently take far too long to amortize itself.

The logical Solution seems to be to rework the cobalt residue with the machinery and equipment that is already installed at this plant, and to employ hydrometallurgical technique with which the operating crews are familiar. With these two premises in mind the entire investigation was conducted.

Report on the Proposed Metallurgy for the

Retreatment of Cobalt Residue

OBJECT: To develop a metallurgical procedure whereby the cobalt residue might be retreated profitably for the recovery of cobalt, cadmium and zinc.

GENERAL PROCEDURE: In order to conform with electrolytic zinc plant practice and technique, this problem was attacked from a hydrometallurgical standpoint only. No procedure involving pyrometallurgy was investigated, so that it is not known to what extent controlled roasting of the cobalt residue would have affected the recovery or costs.

The scheme outlined on the following pages was designed to meet a particular set of conditions, and while it is not submitted as the ultimate, it does possess the advantages of being suitable to the machinery and equipment found at this plant.

PLAN: Expressed in the simplest form the plan involves,

(1) Leaching the material, followed by filtration.
(2) Purification of the solution.
(3) Addition of zinc dust to recover sponge cadmium.
(4) Precipitation of cobalt with sodium hypochlorite.

A more elaborate outline of the plan is given below:

(1) Leaching the air-oxidized Cobalt Residue with 25% - 35% sulphuric acid to produce, after filtration,

   (a) Solution containing the extracted Co, Cd and Zn; with Fe, Al, Mn as the maih impurities.

   (b) A leach residue containing the Sb and most of the Cu, (depending upon the leach procedure), which probably could be sold for either its Sb or Cu content.

(2) Purifying the solution (1-a) to remove the Al and Fe, this process to yield upon filtration,

   (a) Pregnant solution containing Co, Cd and Zn.

   (b) A purification residue containing Al, Fe, MnO_2 and zinc; the latter in sufficient quantities to justify it being fed back into the regular zinc plant leach.

(3) Agitating the solution (2-a) with zinc dust for the recovery of sponge cadmium, followed by filtration to yield,

   (a) Solution containing Co and Zn.

   (b) Sponge cadmium for cadmium electrolysis.

(4) Precipitation of cobalt from solution (3-a) using sodium hypochlorite, to yield, after filtration,

   (a) a marketable product containing mostly cobalt hydroxide with some cobalt oxide.

   (c) Solution low in cobalt and relatively high in zinc which might be sold as zinc sulphate or used as a basis for,

(5) Manufacture of calcined pigment or uncalcined raw material for Rinmann's Green.

Leaching

The object of leaching in this plan is to obtain maximum extrac- ion of the cobalt, cadmium and zinc from the cobalt residue, leaving as uch as possible of the antimony and copper in the leach residue.

Repeated attempts to use the leaching process for solution purif- cation purposes (other than copper removal) were unsuccessful. The rincipal elements to be eliminated from the solution were copper, iron, anganese and aluminum.

The removal of copper was accomplished by the addition of zinc ust to the slightly acid leach, before filtration. Despite the fact that his procedure affected the cadmium extraction adversely, it was thought est to eliminate the copper at this point in order to avoid an extra filtra- on. The problem of copper removal is not a hard one and the question of hether to throw it into the leach residue or make a separate cement copper roduct is one which can be decided during plant operation. In all probab- ity the high antimony leach residue can be sold. If purchasers insist on aving this residue substantially copper-free, then the production of high- rade cement copper might pay for the extra filtration

In the case of iron and manganese both elements required oxidation. e extreme "reducing power" of the leach pulp caused it to consume oxidizers s fast as they could be added - probably due to the action of Sb_2O_3 going o Sb_2O_5. No leach was carried to complete oxidation; that is, until every- hing present had been converted to the higher valances. They were carried ar enough, however, to show that oxidation in the leach was an uneconomic rocess. Even blowing air in a continuous stream through the leach from tart to finish failed to oxidize the iron or manganese. The introduction air, in those cases where very little copper was dissolved, did improve he extraction of cadmium to a marked degree.

The case of aluminum presented a new problem. The discovery and nfirmation of thix element in the cobalt residue will be discussed under rification. Suffice to say here that attempts to run the leach basic with eed, in order to eliminate aluminum, were unsuccessful. Some Al was precip- tated but the amount removed did not justify the loss in extraction. The rocedure of adding zinc oxide (calcine) to the leach to precipitate Al was scarded for three reasons; (1) It made the leach filter poorly, (2) tied the zinc in an unrecoverable form, and (3) diluted the leach residue with nc for which a penalty might be charged when the residue was sold.

Practically no antimony or arsenic gets into the leach solution, the removal of these elements is not a problem. Considerable nickel ssolves if it is present in the feed. Some of this will come out with the dmium sponge - the rest will go through to the barren solution. None gets to the final cobalt oxide product.

On the following pages will be found the leaching experiments and e results. In each case the log of the leach and other significant data e given. All leaches were run on the same general plan of adding the dry sidue, ground to pass ten (10) mesh, to the mechanically agitated acid lution until the final acidity was low enough to allow filtration.

Leach No. 1

Straight Leach. Run for extraction data.
Using 2000 cc of Zinc Plant Electrolyte at 269 gr. acid/L & 52.0 gr. Zn/L.

Tim

Time	Acid Gr/L	Wet Residue added in grams	Water added in cc	T ° C.
9:15 A.M.	269	100		25
9:30		100		47
9:45		100		72
10:00		100		80
10:15		100	100	
10:30		100	100	
10:45		100		
11:00		100		
11:15		100	100	82
11:30		100		84
11:45		100		
12:15 P.M.	9.0			
12:30		25	100	
1:00	4.0			
1:15		15		
1:45	2.0		100	
2:00		10	100	80
2:30	0.5			
2:45				

3:00 Specific Gravity of Solution - 1.478 (Filtered)
Leaching time - - - - - - - - 5 hrs. 45 min.

Leach No. 1 Balance

Product		Zn %	Zn Gr	Cu %	Cu Gr	Cd %	Cd Gr	Co %	Co Gr	Sb %	Sb Gr	Al %	Al Gr
Feed	1150 gr	30.4	350	1.5	17.2	2.4	27.6	3.4	39.1	8.5	98	1.05	12.1
Residue	254 gr	1.8	4.7	7.2	18.3	2.3	5.9	0.13	0.3	38.2	97	0.05	1.3
Electrolyte	2000 cc	52.0	104										
Solution	2640 cc	170	448	.020	.053	9.0	23.7	14.45	38.2	0.31	0.82	4.2	11.1
EXTRACTIONS		98.7%				78.6%		99.3%					

Remarks: Good extraction for Zn and Co but Cd extraction is disappointing. Note that most of Cu and Sb remains in the residue.
Leach filters well.

Leach No. 2

Attempt to precipitate Fe during leach, using $KClO_3$ in acid solution, then adding $CaCO_3$.

Start Leach with C. P. Sulphuric acid instead of electrolyte. (1500 cc)

Time	gr/L Acid	gr Feed	Water	T °C	$KClO_3$	$CaCO_3$	Fe gr/L
8:30 A.M.	250	100		50			
8:50		100		75			
9:10		100		80			
9:30		100		82			
9:50		100	100				
10:10		100	100				
10:30	65	150					
10:50		50					
11:10		50	100				
11:30	25	50					
11:50		50					
12:10 P.M.					2		
12:30		25					
12:50		25					
1:10	1	25					
1:30				80			
1:50		25			2		1.25
2:10		25	100				
3:30							
3:45-	Faintly Acid						
Let stand overnight							
8:30 A.M.	Acid Spot						
9:30		100	100	75	2	3	1.25
10:00	"					3	
11:30	"					3	1.25
1:00 P.M.	"			80	2	3	1.25
3:30	Acid Spot						

Filtered - fair,
Sp Gr 1.480
Leaching time 7 hrs. 15 min.
Agitation for Fe 7 hrs. 0 min.

Leach No. 2 Balance

Product		Zn		Cu		Cd		Co	
		%	gr	%	gr	%	gr	%	gr
Feed	975 gr	30.4	296	1.5	14.6	2.4	23.4	3.4	33.2
Residue	297 gr	5.6	17	4.2	12.5	1.9	5.6	0.73	2.2
Solution	1450 cc	156	226	0.8	1.1	11.0	16.0	18.9	27.4
(Est.) Wash Water	1000 cc		53		1.0		1.8		4.6
EXTRACTIONS			94.2%				76.0%		93.5%

Remarks: Unsuccessful for precipitation of Fe.
The addition of 4 gr $KClO_3$/L had no effect on the iron, indicating that the oxidizer is being consumed by something other than ferrous ion.

Cd Extraction is poor. Filtration is poorer than #1. Using 25% C P H_2SO_4 instead of electrolyte gives a solution a little higher in cobalt but weaker in Zn.

Leach No. 3

An attempt to precipitate Fe and Mn during the leach by adding, as oxidizer, sodium hypochlorite containing sufficient excess sodium hydroxide to satisfy the acid liberated by the Fe and Mn sulphates. Leach neutralized with excess feed before oxidation. Start leach with 1000 cc zinc plant electrolyte.

Time	gr Feed	gr/L Acid	cc Water	T °C
10:15 A.M.	100	271		45°
10:30	100			
10:45	100		100	80°
11:00	100			
11:15	100			
11:30	50		100	
11:45	25	1		
12:00	25			
1:00 P.M.	25	F.A.		
1:30	15	"		
2:00	10	"	100	
2:30	10	"		
3:00	10	"	100	
3:30	10	Neutral		
4:00	10	"		

Stand overnight on steam table

(hypochlorite used contains 120 gr NaOH/L and 43.4 gr Cl_2/L)

	cc Solium hypo-chlorite	gr/L Fe	gr/L Mn	gr/L Al
8:00 A.M.		1.08	1.74	High
9:00	115 cc			
2:00 P.M.		0.80	1.70	Approx 50% removed
Stand overnight on steam table				
9:00 A.M.	100 cc			
1:00 P.M.		0.05	1.20	nil
1:30	25 cc			
2:45		0.05	0.20	nil

3:00 Filtered - very poorly,
Add "Filter-aid" in attempt to speed filtration

Remarks: The leach is successful from a standpoint of Fe and Mn removel but the procedure followed is impractical from an operating point of view because:

1. Filtration is very poor. (see below)
2. Dilution by oxidizing reagent is 25% of the original volume.
3. Fe and Mn oxididation requirements for this solution are 2.95 gr of Cl_2 but their removal took 10.4 gr Cl_2 - only 28% efficiency - again pointing to the consumption of oxidizer by the leach pulp.
4. Fe & Mn basicity requirements for the solution are 4.76 gr NaOH but their removal took 29 gr - only 16% efficiency. (see below)

Leach No. 3 (Cont)

This leach was the first to point to the presence of Al in the leach solutions. The fact that it was difficult to run neutral indicated that some element might be precipitating upon the addition of the feed and liberating sulphate ions. Also it did not seem reasonable to attribute the very poor filtration to the 1.08 gr Fe and 1.74 gr Mn that were precipitated. The slowness suggested some gelatinous substance such as silica, or perhaps beryllium or aluminum hydroxide which might be precipitated upon the addition of the excess caustic in the hypochlorite.

By analyzing the reserve samples of leach solution, and observing the decrease in the bulk of the precipitate formed when successive samples were made ammoniacal, the aluminum was estimated. Precautions were taken to eliminate the possibility of confusing the precipitate with manganous hydrate.

Leach Nos. 4 & 5

Attempt to improve extraction of Cd by blowing air thru leach.
Nos. 4 & 5 were run side by side to determine the effect of using excess residue.
No. 4 was run to a faintly acid condition.
No. 5 was run as basic as possible using feed; the drop in Al was observed and the inability of the air to oxidize iron in neutral solution noted. Leach started with 2000 cc C.P. H_2SO_4 at 275 gr/L.

				No. 4				No. 5			
Time	T °C	gr/L Acid	Water Added	#4 Feed	gr/L Fe	gr/L Mn	Al	#5 Feed	gr/L Fe	gr/L Mn	Al
8:20 A.M.	60	275		100				100			
8:45	72			100				100			
9:00	80			100				100			
9:15	82			100				100			
9:30				100				100			
9:45				100				100			
10:00				100				100			
10:15		53	100	100				100			
10:30				100				100			
10:45			100	100				100			
11:00		8		100				100			
11:30				25				25			
11:45		1	100	15				15			
12:00		FA		None			High	10			High
1:00 P.M.		FA						10			
1:45		"						10			
2:15		Neutral						15			
2:45		"						15			
3:30	80	"		Filtered	1.50	.350		15			
4:00								Let Stand Overnight	1.400	.370	
9:00 A.M.								10			
	All day agitation with air blowing thru solution										
3:00 P.M.								Filtered	1.600	.522	Lower but not appreciably removed

Balance Leach No. 4

Product	Wt.	Zn %	Zn Wt	Cu %	Cu Wt	Cd %	Cd Wt	Co %	Co Wt	Al %	Al Wt
Feed	1140 gr	30.4	347	1.5	17.1	2.4	27.4	3.4	38.9	1.05	12.0
Residue	222 gr	3.5	8	7.2	16.0	0.2	0.4	0.44	1.0	0.2	0.4
Solution	2060 cc	170	350	0.2	0.4	11.6	22.0	21.3	44.0	5.4	11.4
EXTRACTIONS		96.5%				98.5%		97.4%			

Air turned on at this point - continued until filtration.
All solution assays given in gr/L.

Leach Balance No. 5

Product	Wt.	Zn		Cu		Cd		Co		Al	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
Feed	1225 gr	30.4	372	1.5	18.4	2.4	29.4	3.4	40.4	1.05	12.8
Residue	271 gr	4.7	13	6.7	18.1	0.9	2.4	0.56	1.5	0.6	1.6
Solution	2200 cc	170	374	0.2	0.4	12.0	26.2	21.0	46.6	5.0	11.0
EXTRACTIONS		96.5%				91.8%		96.2%			

Remarks: Filtered well. Successful for improving the Cd extraction. It is difficult to run the leach basic with feed - a pH of 4.7 is about the lowest acidity reached.

Unsuccessful for precipitation of iron - all day agitation with an air stream blowing thru the hot solution failed to lower the iron.

Even though #5 had 7.4% more feed than #4, this excess failed to drop the Al appreciably. The small drop in Al does not justify the loss of Cd & Co extraction.

Leach Nos. 6 & 7

Attempt to precipitate iron and manganese during leaching process with $KMnO_4$ as oxidizer plus ZnO. Used 2000 cc C.P. acid at 265 gr/L, and air to get maximum Cd extraction.

No 6

Time	gr Feed	gr/L Acid	T °C	cc Water	gr KMnO4	gr ZnO	gr/L Fe	gr/L Mn	Al
1:45 P.M.		265	55						
to									
3:05	1000	Neutral	80	300					
4:00	Let Stand over night						1.75	0.600	High
9:00 A.M.			80		6				
9:10						40			
0:10	Sampled						1.65	1.560	Lower
1:15						15			
1:45 P.M.	"						1.40	1.560	Very Low
2:00						10			
2:15					10				
4:00	Let Stand over night								
8:00	Agit.								
9:00	Sampled						0.350	2.56	
0:00	Filtered, vol.= 2050 cc								

Remarks: Poor filtration.
Unsucessful. Iron is removed fairly well after 27 gr ZnO/L have removed most of the Al but too much oxidizer is consumed for the results achieved. The manganese continues to climb instead of being eliminated, pointing again to consumption of oxidizer by the leach pulp. The permanganate is being reduced to $MnSO_4$.

Leach #7

As a confirmation, Leach No. 6 was repeated, using 110 gr zinc plant calcine in place of C.P. ZnO. This exhibited the same trend. Fe ended at 0.350 gr/L and manganese in solution ended at 3.28 gr/L.

Leach No. 8

OBJECT: To determine the need for purification of leach solution before precipitation of cobalt.

PROCEDURE: Leach cobalt residue for maximum extraction, then precipitate cobalt and accompanying element with sodium hypochlorite.

Start with 2000 cc C.P. H_2SO_4 at 35% acid.

Zinc dust added to precipitate copper with leach pulp. Used new batch of feed. (#2)

Time	Temp. C.	Water added cc.	Acid gr/L	Feed gr	Zn Dust gr	
8:30 A.M.	76		350	400		Turned air on at start
8:45	88	250		400		
9:00				400		
9:10		250	75			
9:20				400		
9:40		250	1	20		
10:20						Cu 7.8 gr/L
10:40						Turned off air
10:50		250			23	Add Zn dust to precipitate Cu
12:30 P.M.						Filter Filters well

Solution 2900 cc
Sp. gr. 1.440

Leaching time - 2 hrs. 10 min

LEACH BALANCE #8

Product		Zn		Cu		Cd		Co		Al		Sb	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
Feed	1620 gr	29.5	478	2.0	32.4	2.5	40.5	2.7	43.7	1.38	22.4	7.3	118
Residue	425 gr	2.5	11	5.2	22.1	1.9	8.1	0.19	0.8	0.2	0.8	27.5	117
Sol'n.	2900 cc	156	453	3.1	9.0	10.5	30.5	15.0	43.5	7.1	20.6	.020	0.06
Dust			22										
F. Water (Est.)	1000 cc		36				1.0		1.0		1.0		

Extraction 97.5 80.0% 98.1%

Leach No. 3 - con'd.

The precipitation of cobalt will be discussed under cobalt oxide production.

This leach brings out some interesting points in regard to what might be encountered in re-working residue of this character which is not uniform as to metallic content or degree of oxidation.

A new batch of feed was used, taken from different portions of the storage pile. Unlike the first batch, this material yielded a solution very high in copper. It is not known whether this was due to the effect of air blowing in from the start, or whether the copper would have dissolved unaided, because of the high (350 gr/L) acid at the start.

Despite the high copper in solution the cadmium extraction is disappointing. This may be due to not having allowed enough time during the leaching period for the cadmium to dissolve. It is barely possible that the Zinc dust added precipitated Cadmium, and this cadmium was not allowed time enough to displace copper.

A theoretical quantity of zinc dust is not sufficient to completely precipitate all the copper. Adding 23 gr dust on the basis of 1.03 gr Zn dust precipitating 1 gr copper, still left over 3 gr copper in solution.

Almost all the Al dissolves and will have to be removed from solution.

Practically all of the Sb stays with the residue.

Leach No. 9

Object: To leach as in No. 8 then observe the effect of adding zinc dust to completely precipitate the copper.

Start with 2000 cc C P H_2SO_4 at 357 gr/L - air blowing in from the start.

Time	Temp. °C	cc H_2O	gr Feed	gr/L Acid	gr Zn Dust	gr/L Cu	REMARKS
9:00	75	250	400	357			Turned on Air
9:15		250	200				
9:30		250	200				
10:00		250	200				
10:15				105			
10:30		250	200				
10:45	80	250	200				
11:00				40			
11:15			100				
11:30			100				
11:45			80				
11:55						9.3	Turned off air
1:00							Filtered 100 cc sample of leach sol'n and pulp (1st Residue)
2:00	65				30		
4:00						1.6	Let stand over-night
9:00	50				5		
10:00						1	
10:15					5		
10:45						0.25	
11:00					5		
11:30						0.15	
12:00	55						Filter

Filters well.
Leaching time, 2 hrs. 45 min.
Cu ppt. time, 5 hours.

BALANCE LEACH #9

roduct		Zn		Cu		Cd		Co		Al		Sb	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
eed	1640 gr	29.5	485	2.0	32.8	2.5	41.0	2.7	44.2	138	22.6	7.3	120
t Residue	14.8 gr	2.5	0.4	3.3	0.5	0.7	0.09	0.12	0.01	0.40	0.06	33.5	5x
ain Residue	418 gr	3.2	13.4	7.5	31.3	1.8	7.51	0.16	0.67	0.57	2.38	31.4	125
inc Dust	40		40										
ol'n, incl. sh Water	3000 cc			0.150	0.4	10.2	30.6	14.5	43.5	6.67	20.0		Tr

XTRACTIONS: 97.4 81.4% 98.5%

x Sb in solution .015

xx Sol'n assays always given in grams per liter.

Leach No. 9 (Cont)

This leach would indicate two things:

1. A short leach of 3 hours is sufficient to extract the greater portion of the cadmium.

2. The additions of zinc dust, to precipitate copper, are responsible for the poor cadmium extractions.

Notice that the 1st residue (before the zinc dust was added) contained only 0.7% Cd. Assuming that the main residue would have weighed 420 grs. had the zinc dust not been added nor the 1st residue removed, then the cadmium extraction, calculated on a 0.7% Cd basis, would have been about 93%.

This material seems to take about 50% dust in excess of the theoretical to get all the copper. This excess, over what was added in No. 8, did not effect the cadmium extraction adversely - an 81.4% on No. 9 compares favorably with an 80.0% on No. 8.

The Leach solution No. 9 was given a treatment with calcine to remove Al. The data and discussion will be found under "Purification".

Leach No. 10

Objects: To leach same material as in No. 9 (batch #2) but withhold air until acid is very low, to observe the effect in regard to amount of copper dissolved.

To determine the effect of adding calcine to remove Al, before leach is filtered.

Air blowing thru to attempt to remove iron. No zinc dust added. Start with 2000 cc C P H_2SO_4 at 357 gr acid/L.

Time	°C Temp	cc H_2O	gr Feed	gr/L Acid	gr Calcine	Al	REMARKS
9:00 A.M.	70		400	357			(No Air)
:15		250	200				
:30	60	250	200				
:30		250	200				
:15				90			
:30		250	200				
:45		250	200	30			
:			100				
:30			30				Cu = high
:45		250					Turn on Air
:00 P.M.							Filtered 100 cc sample of pulp and solution (1st Residue)
:10						6.7	Cu, 8.1 gr/L
2:00					180		
:00						2.9	Let stand overnight
:00 A.					30		Turn on Air again
:00						1.0	
:00							To filter

Filters very poorly.
Fe in Sol'n., 2.3 gr/L
Cu in Sol'n., 4.6 gr/L
Leaching time, 2 hr 45 min
Al ppt. time, 4 [illegible]

BALANCE #10

roduct		Zn		Cu		Cd		Co		Al		Sb	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
eed	1580 gr	29.5	466	2.0	31.6	2.5	36.0	2.7	42.6	1.38	21.8	7.3	115
t Residue	15.5 gr	2.2	0.3	2.4	0.3	0.3	0.04	0.19	0.03	0.19	0.03	21.4	3.2 x
nd Residue	548	10.7	58.6	3.1	17.0	1.8	9.86	0.16	0.88	2.7	14.7	20.1	115
lcine	210	56.0	115	0.3	0.6	0.3	0.6			0.1	0.2		
olution	3000 cc	155	465	4.9	14.7	8.0	24.0	13.8	41.4				Tr
TRACTIONS:		90.0				74.4%		97.4%					

x Sol'n Sb 0.10

xx Assays in grams per liter.

Leach No. 10 (cont)

This leach demonstrates again (See No. 4) that it is impossible to precipitate Fe during leaching process using air in neutral solution so long as there is any Al present. The Al assays given on solution are approximations only, estimated from the observed bulk of precipitate formed in an ammoniacal solution. As much as 70 gr Calcine/L were not particularly effective in removing the Al. The filtered solution was given a treatment with C.P. ZnO and air which did remove most of the iron and all of the aluminum. (see under "Purification")

This material would give a high copper solution without the use of air.

The surprising thing about the calcine addition is that it removed over 50% of the copper from solution, probably as $Cu(OH)_2$.

Unfortunately it also ruined the Cd extraction. As shown by the 1st residue assay of 0.3% Cd if we assume the main residue weight would have been 400 grams without the addition of the calcine, then the Cd extraction can be calculated to be about 99%. These residue assays were carefully checked and found to be correct. It is not known in what form the cadmium was precipitated, but it is known that it was not due to the formation of a copper-cadmium complex. The residues from the calcine treatment of leach solutions No's. 9 and 10, for the removal of Al, were carefully tested for cadmium and found to be "nil", although No. 10 had a high Cu content. Evidently the addition of ZnO to these cadmium bearing solutions will not precipitate Cd when the ZnO is added away from the leach pulp.

It does not seem advisable to add the calcine before filtration. From the assays of Leach No. 9 it is reasonable to assume that the main residue has been raised in Zn content from 3% to 10.7% by these additions. It is estimated that 50% of the 118 gr of Zn added with the calcine went into the solution as $ZnSO_4$.

The leach filtration was poor.

Leach No. 21

This leach was run mainly in order to obtain solution from a portion of the original batch (#1) of residue used in leached 1 to 7 incl., air blown on from the start to compare with leaches 8 and 9. Notice that very little copper dissolves with this material. Run in a lead pot instead of a glass beaker:

Start with 6 litres of C P H_2SO_4 at 310 gr acid/L/

Time	°C Temp	cc Water	gr Feed	gr/L Acid	REMARKS
10:15 A.M.	50		500	310	Turn on air
10:30			500		
10:45	63	250	500		
11:00	69		500		
11:15			500		
11:45	77	250	500	20	
12:00 Noon			50		
1:00 P.M.			50		
1:25	64		50		
1:30			50	1	
3:00					Filter. Vol = 7000 cc incl. W. W. Sp. Gr. = 1.450. Leaching time = 4 hours - 45 minutes.

BALANCE

duct		Zn		Cu		Cd		Co		Sb		A	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
d	3700 gr	30.4	1140	1.5	55.5	2.4	88.8	3.4	125.8	8.5	314	1.05	38.9
sidue	830 gr	2.0	17	6.5	54.0	1.4	11.6	0.5	4.2	38.0	316	0.3	2.4
lution	7000 gr	160.0	1120	0.2	1.4	11.0	77.0	17.2	120	.020	0.14	5.3	37.1

RACTIONS 98.6% 86.9% 96.8%

Leach No. 24

The material for this leach was a new batch (#3) of fresh cobalt residue taken from the storage bin under the Shriver press. It was thoroughly dried in the air for two weeks at an even heat of 30°C to 35°C, then crushed, rolled and sampled. It differs from the other batches in being much higher in Cu and Co and low in Al.

The leach was run to obtain solution which was high in cobalt.

Start with 8 litres of 350 gr C P H_2SO_4 in a lead pot.

Time	cc Water	°C Temp.	gr Feed	gr/L Acid	REMARKS
9:30 A.M.		60	2500	350	No air.
10:00	500			240	
10:10		78	2500		
10:45	500			140	
10:50			2400		
11:30	1000			60	
11:40			1000		
12:00 Noon	500			25	Turn on air.
1:00 P.M.	500	81		22	
1:05			1000		
1:30	500			5	
1:40			500		
1:50				- 1	
2:30					Start filtration - good Leaching time - 6 hours. Vol. of Sol'n plus wash water 15330 cc. Sp. Gr. = 1.450

Balance Leach No. 24

		Zn		Cu		Cd		Co		Al		Sb	
oduct		%	Wt.	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
ed	9900 gr	19.5	1930	14.2	1408	2.2	218	7.3	723	0.24	23.9	3.8	376
sidue	3340 gr	1.1	34	42.0	1400	0.2	6	0.6	19	0.10	3.3	11.3	378
lution ncl W. ter)	15330 cc	130	1995	0.65	12	14.5	222	45.2	700	1.34	20.6	.020	0.3
TRACTIONS			98.2%				97.3%		97.3%				

x Solution assays in grams per litre.
Very little copper dissolved using batch No. 3

Leach No. 25

OBJECT: To leach with zinc plant electrolyte instead of C.P. H_2SO_4.

Used another batch (#4) of cobalt residue from storage bin, thoroughly dried, high in cobalt.

Time Time	Temp °C	Water cc	Feed gr	Acid gr/L	Electrolyte cc	REMARKS
9:40 A.M.	50		1000	230	10000	Turn on air.
9:50			1000			
10:00	70		500			
10:15			500			
10:30	75	1000	500			
10:45			500			
11:00			500			
11:15	80		500			
11:30			500			
11:40				20		
11:50		1000			1000	
12:00 Noon				40		
12:15 P.M.		1000	500			
12:30			500			
12:45			500			
1:00	78		500			
1:15				20		
1:20					1000	
1:30		1000	500			
1:45			500			
2:00			352			
2:15				1		
2:40						Filter

Filters fair.
Vol. = 17700 cc
Sp. Gr. = 1.450
(Fe 1.3
(Mn 1.49. Leaching time, 5 hours.

BALANCE LEACH NO. 25

Product		Zn		Cu		Cd		Co		Sb		Al	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
Feed	8052	21.0	1860	14.7	1301	2.7	239	9.0	796	3.2	284	0.85	75.3
Electrol.	12000 cc	49.3	592										
Residue	2891 gr	2.3	67	41.5	1200	0.7	20	0.66	19	9.9	286	0.1	2.8
Solution	17700 cc	132	2340	5.75	102	12.2	216	43.3	766	.020	0.35	4.1	72.6
Wash Water (Estimated)	2300 cc		45		1		3		11				1
EXTRACTIONS		96.4%				91.7%		97.5%					

x Solution assays in grams per litre.
Considerable copper dissolves using batch #4.

Leach No. 30

Run to determine the feasibility of leaching the fresh cobalt residue before it has been oxidized. Taken directly from top of storage bin - most recent residue made.

10:00 A.M.	Start with 8000 cc of C P H_2SO_4 at 356 gr acid/L. 60°C
10:00 A.M. to 3 P. M.	Feed in 14478 gr of wet residue by mulling small portions with water in iron mortar then adding to leach as paste. (14478 gr wet feed at 37.7% moisture equals 9000 gr dry feed)
3:10 P.M.	Acid 35 gr/L T 82°C
3:20 P.M.	Add 2000 cc Water
3:40 P.M.	Acid 31 gr/L
3:50 P.M.	Add 1000 cc Water
9:00 P.M.	Acid 31 gr/L. (no change in acidity after 5 hrs. agitation)
9:05 P.M.	Add 2000 cc Water-T 85°C
9:10 P.M.	Samples - obtained 1st residue put solution back into leach.
9:15 P.M.	Turn on air and let agitate overnight
8:00 A.M.	Acid 30 gr/L (1 gr/L drop after 11 hrs. agitation with air) At this point it was considered impossible to neutralize the leach, with feed, down to an acidity acceptable for filtration. Further additions of the paste would result in a pulpy mass which would hardly agitate.
9:00 A.M.	Add 610 gr zinc plant calcine to neutralize leach. (Not added to precipitate Al)
10:00 A.M.	Acid 0.8 gr/L Filter: Filters well. Sp Gr = 1.400. Vol 15200 cc

Balance Leach No. 30

Product		Zn		Cu		Cd		Co		Sb	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
ed	9000 gr	17.5	1575	22.6	2040	1.8	162	8.7	783	4.2	378
cine	610 gr	55.3	338	0.2	1	0.3	1.8				
t Residue	297 gr	1.4	4	47.0	140	0.05	0.15	11.2	33	8.8	26
in Residue	4335	2.5	107	43.7	1890	0.05	2.1	8.1	351	8.0	346
l'n. Incl. W. ter	15200 cc	117	1790	0.005	0.08	10.5	160	26.0	395	0.005	0.08
XTRACTIONS		94.2%				98.5%		51.0%			

x Solution assays in gr/L

Not successful for cobalt extraction.

This cobalt residue sample, perhaps, does not reflect the analysis of the usual fresh residue made, but it is representative of the type of unoxidized material which would be encountered.

The poor cobalt extraction (51%) is probably explained by the residual active zinc dust present in the feed. As the leach approached low acidity the dust precipitate cobalt from solution.

The 1st residue, before the air was admitted, was 11.2% Co, and after all night agitation and neutralization with calcine the main residue had 8.1% Co. Both of these products are too high to discard, so attempts to retreat the leach residue #30 were made.

Leach 30 A

Retreatment by leach Res. #30 with acid leach.
Residue has been thoroughly dried and oxidized.
Start with 1000 cc C P H_2SO_4 at 250 gr acid/L.

Time	Temp °C	Feed gr	Acid gr/L	REMARKS
8:00 A.M.	57	100	250	
8:10		100		
8:20		100		
8:30		100		
8:40	80	100		
8:50		100		
9:00			Neutral	Add 1 litre of 25% C P H_2SO_4
9:10			45	
10:15			41	
10:20		100		
10:30		20	2	
10:45	85	20		
11:00		20	Neutral	
12:00 Noon				Filtered. Filtered well. Vol. = 2400 cc. Sp Gr = 1.300

Balance - Leach No. 30 A

Product		Cu		Co	
		%	Wt	%	Wt
Feed	760 gr	43.7	332	8.1	60.7
Residue	350 gr	21.6	76	1.25	4.4
Solution	2400 cc	107	257	23.6	56.7
EXTRACTION					92.7%

Successful for cobalt extraction but impractical for plant operation because of the high Cu content of the solution. The problem of Cu removal from the solution will be considered under leach No. 40.

Leach No. 30 B

Retreatment of leach residue 30 with hot water leach.
Start with 2000 cc water.

Time	Temperature °C	Feed gr
9:00	62	100
10:00	72	100
11:00	75	100
12:00	80	100
1:00	78	100

4:00 Filtered. Vol. 1700 cc.

Balance
Leach No. 30 B

		Cu		Co	
		%	Wt	%	Wt
Feed	500 gr	43.7	219	8.1	40.5
Residue	490 gr	43.6	213	7.0	34.3
Sol'n (Incl. Wash Water)	2000 cc	3.0	6	3.1	6.2

EXTRACTION 13.8%

Unsuccessful for Co extraction.

Leach No. 40

Object: To obtain a leach solution high in copper, for purification experiments.
Used batch No. 2 (Same as for Leach 8, 9, & 10)
Start with 6 L of C P H_2SO_4 at 348 gr/L.

Time	°C Temp.	gr Feed	gr/L Acid	cc Water	REMARKS
8:50 A.M.	60	200	348		
9:00	63	200			
9:10	68	200			
9:20	72	200			
9:30	75	200		500	
9:40	77	200			
9:50	77	200	210		
10:00	78	200			
10:10	78	200			
10:20	79	200			
10:30	79	150	170		
10:40	79	150			
10:50	79	150		500	
11:00	79	150			
11:10	79	150			
11:20	80	150			
11:30	80	150			
11:40	79	150		500	
11:50	79	150			
12:00 Noon		150			
12:10 P.M.		200			
12:30		200		500	
1:00	78	150			
1:10		100	34		Turn on Air.
1:15		100			
1:20		100			
1:25	78			500	
1:30		100	14		
1:35		50			
1:40		50			
1:45		50	4	500	
1:50		50	Neutral	1000	Filtered well. Sp.Gr.= 1.446. Vol. 8900 cc including wash water.

Balance
Leach No. 40

		Zn		Co		Cd		Cu		Al	
		%	Wt	%	Wt	%	Wt	%	Wt	%	Wt
ed	4650 gr	29.5	1372	2.1	97.8	2.5	116.2	2.7	125.6	1.38	64.2
es.	1115 gr	2.0	22	2.1	23.4	1.0	11.2	0.18	2.0	1.6	17.[illegible]
l'n.	8900 cc	152	1352	8.5	75.6	11.3	101.0	13.8	123.0	5.2	46.3
XTRACTIONS		98.4%				90.4%		97.6%			

x Solution assays in grams per litre.

Leaches

All these leaches were run with a standard procedure of adding the cobalt residue to solutions of sulphuric acid until a low acidity was obtained, blowing in air to help Cd extraction, then , finishing off with feed to an acidity low enough for filtration (about 2 gr acid per litre, or less).

No.	Type	Acid		gr Total Acid	Total Feed	Batch No.	Soln Vol. cc	Solution Assays gr/L				
		cc Volume	gr/L					Sp Gr	Fe	Mn	Al	Co
11	C.P.H_2SO_4	2000	252	504	1040	1	2200	1.416	1.6	0.66	4.8	15.8
12	"	2000	249	498	1040	1	2010	1.452	1.6	0.68	5.0	17.8
13	"	2700	261	705	1450	1	2700	1.450	1.5	0.52	5.1	17.5
14	"	2700	262	708	1450	1	2800	1.460	1.5	1.52	5.1	17.3
15	"	5400	275	1485	2150	1	6200	1.440	1.5	0.59	5.0	16.0
18	"	3000	282	846	1720	1	3200	1.470	1.5	0.6	4.5	17.4
22	"	7000	297	2079	4300	1	7600	1.510	1.7	052	4.8	17.5
26	Elect	4000	267	1068	3600	3	6650	1.460	2.75	1.94	4.0	39.2

Purification

The term "Purification" is in this plan refers to the precipitation of aluminum and iron from the filtered leach solution. Manganese may be removed, as desired, and some copper, if present is removed incidental to the treatment for Al and Fe.

The need for purification is three fold. First, and most important, is the necessity of removing aluminum. The removal of Fe, Mn or Cu is a question of economics but the precipitation of Al into the purification residue is absolutely essential if the plan is to be workable. If the solutions are not first purified of Al, this element will be precipitated by the subsequent additions of sodium hypochlorite and render the final cobalt hydroxide product unfilterable. Secondly, Fe, as well as Al, is precipitated by NaOCl, so that if both these elements are not removed they contaminate the cobalt hydroxide. The final product, being relatively high in impurities, is unattractive to cobalt oxide consumers. Lastly, there is no way to stop the Al or Fe from consuming the reagent intended for cobalt precipitation so nothing in gained by not purifying previous to adding the NaOCl.

Aluminum was first suspected in leach No. 3. Again in trying to purify leaches No. 1 and No. 4 (p1, p4) and again in the cobalt precipitation of leach No. 8 (Prec. No. 1). Its behavior in the solution analysis for Fe was responsible for its discovery. When solutions were oxidized, made ammoniacal and boiled, they were later centrifuged to facilitate the separation between the ferric hydrate and the liquid. The Al present would precipitate along with the iron and form considerable bulk in the bottom of the tube after centrifuging. By observing the decrease in this bulk on samples taken after addition of basic reagents such as ZnO or NaOH, the first clue to its presence was had. At first thought to have been beryllium, or some similar element, it was later confirmed as aluminum by the Gooch and Havens test which consists of passing gaseous hydrochloric acid into a cold, concentrated solution of the metal chlorides, in a mixture of ether. Beryllium remains soluble while aluminum is precipitated as $AlCl_3 \cdot 6H_2O$.

The removal of Al from the leach solutions necessitated the addition of some basic reagent to precipitate $Al(OH)_3$. The basic reagent most suitable was ZnO, as it was cheap, did not precipitate cobalt, nor lose the sulphate ion as an insoluble coupound. The sources of ZnO available to this plant, other than commercial ZnO purchased in the open market, are zinc plant calcine and zinc melting furnace dross. If the final zinc sulphate solution is to be sold or used in the manufacture of some product it is advantageous to conserve the sulphate ion in the solution, which it would be according to the reaction:

$$Al_2(SO_4)_3 + 3ZnO + 6\ H_2O \rightarrow \underset{\text{(precipitate)}}{2\ Al(OH)_3} + \underset{\text{(sol'n)}}{3\ ZnSO_4} + 3\ H_2O$$

As the iron is usually present in the leach solution in the ferrous state, it requires oxidation before it can be precipitated. There are very few oxidizers which will work in neutral or basic solutions. The important ones are: Cl_2 gas, hypochlorites, chromates, persulphates, hydrogen, peroxide, sodium peroxide and permanganates.

It was thought best not to consider the Cl_2 gas because of its insolubility in the leach solution and its offensive properties when set free in the air on a large scale. Hypochlorites were tried and found to work, but it was kept in mind that the residue might be returned to the main zinc plant leach. Hence the hypochlorites were not particularly desirable. Chromites were not tried because of the slimey, difficultly filterable hydroxide formed when chromium salts are precipitated by bases. The persulphates were discarded because of their costs.

Sodium peroxide was found to be a good oxidizer for iron but poor for manganese. Hydrogen peroxide was only tried as manganese oxidizer and was found to be unsatisfactory.

Potassium permanganate was found to be a dependable oxidizer for iron, never having failed to precipitate iron under a variety of conditions. It must be remembered, however, that $KMnO_4$ does not have the same oxidizing power in basic solution as it has in acid solution Whereas in acid solution the manganese in permanganate undergoes 5 units of reduction, in basic sol'n it undergoes but 3 units, going from $KMnO_4$ to MnO_2. Thus, the oxidizing power of permanganate in basic solution is but 60% of what it is in acid solution.

Manganese can be eliminated during the purification process, if desired, but unlike iron, this element is not oxidized with Na_2O_2 or H_2O_2 under the conditions found in this process. It can be eliminated down to 75 to 100 mg per litre by permanganate, according to the well known reaction

$$3\ MnSO_4 + 2\ KMnO_4 + 2\ H_2O \longrightarrow 5\ MnO_2 + K_2SO_4 + 2\ H_2SO_4$$

provided there be sufficient zinc oxide present to neutralize the acid.

Repeated attempts to clean the solution of manganese were unsuccessful. In some cases, by adding the theoretical amount of $KMnO_4$ for both Fe and Mn, the manganese could be dropped to a low figure (75 mg/L). However, when an unsufficient amount of $KMnO_4$ was first added and the remaining Mn "titrated" with $KMnO_4$ the results were far from satisfactory. If a drop in Mn occurred at all it did not proceed along stoichiometric lines despite the fact that permanganate was being consumed. Analysis of the purification residue confirmed the belief that the cobalt was being precipitated by this reagent - probably as a cobalt manganate - and being lost in the residue. The $KMnO_4$ which was added for Fe only did not precipitate cobalt.

It was later found out that consumers and processors of cobalt oxide did not regard manganese as a very harmful impurity, and would accept a product, without penalty, which was relatively high in this element. After that, the purification for manganese was considered to be of secondary importance. It should be pointed out that leaching with commercial H_2SO_4 gave a solution which ran approximately 0.4 to 0.7 gr Mn/L; an amount which will not show up over 2% in the final product. If zinc plant electrolyte is used for the leach, the resulting solutions are between 1.0 and 3.0 gr Mn/L and will run the Mn in the final product up to 3.0% or 5% Mn.

Some copper is precipitated - probably as $Cu(OH)_2$ - incidental to the treatment for Al, by ZnO. This amount becomes appreciable if the copper is not removed before the purification in those solutions which assay 5 gr Cu/L or higher. If a few hundred milligrams of copper are left in the leach solution to insure a good Cd extraction, then advantage can be taken of this basic precipitation to further clean the solution of Cu before sponging.

Purification #1

Attempt to precipitate Fe by addition of hypochlorite as oxidizer using $CaCO_3$ for basic reagent.

Use all of solution from Leach #1.

Hypochlorite contained 120 gr NaOH/L and 50 gr Cl_2/L.

Time	Sol'n cc	T °C	Hypo Chlorite cc	$CaCO_3$ gr	Fe	Mn	
9:30 A.M.	2460	60	160 cc	16	1.20	2.24	effervescence
10:00	Sp.Gr. 1.478				1.20	1.26	"
10:45				4			"
11:15				2			"
12:00 P.M.				2			"
1:00				2			"
2:00				2			"
2:15		65		2			"
2:30					0.70	1.20	"
3:00				4			"
3:30				4			"
3:45		60		4			"
Let stand overnight.							
10:00 A.M.	Add 200 cc Water	55			0.70	1.26	
10:30			50				
2:00 P.M.					0.60	%1.30	
3:00	Filtered poorly Vol.=1920 Sp.Gr.=1.510						
9:30 A.M.	Add 300 cc Water	55	50				
10:30					0.03	0.37	
11:45			15				
1:00 P.M.						0.07	
2:00	Filtered poorly						

This purification is based on the principle that sodium hypochlorite will oxidize iron to the ferric state, and precipitate manganese as MnO_2, in basic solution.

It was run before the presence of aluminum was determined. It was thought that a few grams of calcium carbonate, sufficient to care for the acid liberated by the iron and manganese sulphates, would be enough to render the solution basic. For additional basicity there were present about 10 gr free NaOH in the hypochlorate added. (By "free" caustic is meant that which is in excess of the amount necessary to satisfy the Cl_2 in the hypochlorite).

Purification #1 continued

At the temperature of this purification there is an incipient reaction between calcium carbonate and zinc sulphate to yield calcium sulphate and basic zinc carbonate. As this reaction precipitates both zinc and sulphate ions it is undesirable, but for a first trial it was thought that most of the basic carbonate might revert to zinc sulphate upon the precipitation of the iron.

Every addition of $CaCO_3$ produced violent effervescence showing vigorous reaction, and in the light of what we now know, the reaction is believed to have been:

$$Al_2(SO_4)_3 + 3\ CaCO_3 + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ CaSO_4 + 3\ CO_2$$

The removal of Al might have preceded according to the following calculations:

Al Precipitated by 42 gr $CaCO_3$	7.54 gr
" " " free caustic in 1st addition of hypochlorite	2.24 gr
" " " free caustic in 2nd addition of hypochlorite	0.71
	10.49

It is known that the leach solution contained 11.1 gr Al.

The purification was not successful from a practical viewpoint. The $CaCO_3$ would "boil-over" every purification on a plant scale. Some other basic reagent besides $CaCO_3$ is necessary. The free caustic in the hypochlorite is not only too expensive for Al Purification purposes but a slight excess would precipitate $Zn(OH)_2$, a substance very difficult to filter.

Purification #4

This purification was based on the same principle as Purification #1. Sodium hypochlorite was used to oxidize Fe and precipitate Mn. A 50% excess of chlorine over the oxidation requirements for Fe and Mn was added to insure complete removal.

It differs from #1 in that ZnO was used to precipitate the Al and make the solution basic before the addition of the NaOCl.

10:00 A.M.	1000 cc Leach Sol'n #4 at 65°C—Fe 1/5 gr/L—Mn 0.30 gr/L—Al 5.4 gr/L X
10:15	Add 30 gr C.P. ZnO as a thick emulsion in water.
10:45	Add 26 cc NaOCl containing 76 gr Cl_2/L and 120 gr NaOh/L.
11:00 to 1:30 P.M.	Agitation.. While agitating the solution turned brown, then black.
1:30	Sampled. - Fe nil. Mn nil. Al very low. T = 66°C.
2:00	Filtered - With difficulty. Necessary to add 20 gr filter aid to speed filtration.
	Residue - 74 gr total (54 gr without the filter aid). Total residue contained 2.04% Co. (or 1.51 gr Co.)

Discussion: The purification accomplishes its purpose but is impractical not only because of its slow filtration but because of the high percentage of cobalt lost in the residue.

$$\frac{\text{gr cobalt contained in Purification residue } 1.51}{\text{gr cobalt available in 1 liter Solution } 21.3} = 7.1\% \text{ of available cobalt loss.}$$

To account for this loss is not difficult. It was probably due to the excess hypochlorite added. Considered in the simplest terms Fe is oxidized from a valence of two to three and manganese from two to four. Therefore stoichiometrically

55.84 gr Fe will require 35.46 gr Cl (or 1 gr Fe requires 0.633 gr Cl).
54.94 gr Mn will require 70.9 gr Cl (or 1 gr Mn " 1.29 gr Cl).

1.5 gr Fe in 1000 cc solution x 0.633	=	0.954 Gr Cl_2.
0.3 gr Mn " " " " x 1.29	=	0.387 gr Cl_2.
Theoretical Cl_2 requirements for Fe Mn	=	1.341 gr Cl_2.
Added 26 cc NaOCl containing 76 $MgCl_2$/L	=	1.976 gr Cl_2.
Excess Chlorine added		.635
1 gr Co requires		0.601 gr Cl_2.

$\frac{0.635}{0.601}$ 60! = 1.07 = gr Co this excess Chlorine might precipitate at 100% efficiency.
0.69 = gr Co precipitated by $Al(OH)_3$, using the average ratio from Purif. #2 & #3, of 0.12 gr Co precipitated by every 1 gr Aluminum.
1.76 = gr Co which might have precipitated.

That only 1.51 gr Co precipitated instead of 1.76 probably means that the hypochlorite was not 100% efficient.

In plant practice it might be possible to control the hypochlorite additions more closely, thereby avoiding losses of cobalt held in the Purification residue. However, both Purif. #1 and #4 indicate that the additions of Na(OH), even in slight excess, result in an undesirable precipitate, very difficult to filter.

Purification #5

To be compared with #4 & #6 Run on leach 1000 cc solution #11, at 15.8 gr Co/L.

Use ZnO and Sodium Hypochlorite containing 120 gr NaOH/L & 43.4 gr Cl_2/L.

The hypochlorite added on a caustic basis - that is, the theoretical amount of NaOH to satisfy the acid formed by the liberation of the Fe & Mn sulphates was given at each addition and the Cl_2 allowed to oxidize at random.

1 gr Fe requires 2.15 gr NaOH.
1 gr Mn " 1.46 " ".

Time	Temp ° C	Hypo Chlorite added cc	ZnO gr	Fe gr/L	Mn gr/L	Al gr/L
8:30 A.M.	70			1.6	0.66	4.8
8:40			5			
8:50		29				
10:00	67			0.9	0.075	high
11:00			2.5			
11:05		17				
1:00 P.M.	61			0.9	0.75	lower
1:45			5			
2:30				0.05		1.6

3:10 Add 2 gr CaF_2.
3:40 Filtration improved a little.
3:50 Add 1 gr Glue.
4:10 Filtration possible but slow.

Obtained 20 gr residue at 4.73% Co.

$\frac{0.946}{15.8}$ = 6.0% of available Co held in Purification residue.

Purification #6

To be compared with # 4 and #5 Run on 600 cc leach solution #11 at 15.3 gr Co/L.

Use ZnO, and hypochlorite containing 90 gr NaOH/L and 71 gr Cl_2/L. (Very little free caustic in this hypochlorite).

Hypochlorite added on the chlorine basis - that is, the theoretical amount of Cl_2 necessary to oxidize both Fe & Mn was given at each addition and the caustic allowed to precipitate whatever it would.

1 gr Fe requires 0.633 gr Cl_2.
1 gr Mn " 1.29 " "

Time	Temp °C	Hypo cc	ZnO gr	Fe gr/L	Mn gr/L	Al gr/L	
8:00 A.M.	68			1.6	0.66	4.8	
8:10			3				
9:30		16					
9:50				0.44	0.52	high	
10:20			3				
10:30		10					
11:15				0.4	0.075	lower	
11:30		10					
1:15 P.M.				nil	0.050	2.5	

2:00 Filtration impossible.
2:10 Add 2 gr CaF_2.
2:40 Filtration improved slightly.
2:50 Add 2 gr Glue.
3:00 Filtration possible, but slow.

Obtained 13 gr residue at 0.68% Co.

$$\frac{\text{Cobalt in Residue}}{\text{Cobalt available in 600 cc solution}} \quad \frac{0.09}{9.5} \cong$$ 1% of available Co held in Purification Residue.

Purification 4, 5 and 6 show that it is possible, but not particularly desirable to remove the Fe and Mn from solution by means of sodium hypochlorite.

It might have been possible to speed the filtration of No's 5 and 6 by adding enough ZnO to completely precipitate the Al. However, this improvement is doubtful as the free caustic had probably precipitated sufficient $Zn(OH)_2$ or some other hydrate, to ruin the filtration.

Purification #2

Attempt to precipitate Fe from neutral solution using Air as oxidizer. Aluminum removed by use of zinc plant calcine.

Start with 3000 cc of solution from Leach #9. Add calcine as thick emulsion with water.

Time	Temp ° C	Calcine gr	Fe gr/L	Al gr/L	
8:15 A.M.			2.15	6.67	Turn on air.
8:30	78	150			
9:30	78		2.00	high	
9:45		50	1.90	1.0	
10:45	75		1.75	0.2	
11:00		40		"	
12:00 Noon				"nil"	Agitation until 4:00 P.M. with air blowing thru neutral solution. Then stand overnight on Steam table.
9:00 A.M.	70		1.75	"nil"	Turn on air again.
10:00			1.50	"nil"	
12:00 Noon					Filter. Filters well - very large volume of precipitate.

Purification residue obtained 260 grams.

Assays on Residue: Zn - 35%, Co - 0.33%, Cd - less than 0.1%.
Cobalt held in Purif. Residue $\frac{2.3}{43.5}$ = 5.3% of available Cobalt.

Remarks: This purification would indicate that,

1 - Aluminum can be successfully removed from solution by the use of zinc plant calcine.

2 - The air blowing thru a warm solution, made basic as possible with calcine, does not appreciably oxidize iron.

3 - The $Al(OH)_3$ tends to occlude cobalt. The washing of this filter cake required considerable water.

Purification #3

This was run on leach solution #10 to compare with Purif. #2 in order to determine,

1 - If air would oxidize Fe in a solution made neutral with C.P. ZnO instead of calcine, and

2 - If the filtered leach solution could be cleaned of aluminum.

Time	Temp ° C	ZnO gr	Fe gr/L	Al gr/L	Cu gr/L	
8:10 A.M.	77		2.3	2.1	4.7	Turn on air.
8:20		15				
9:20			0.7	0.2		
10:30		10				
1:15 P.M.			0.45	0.1		
1:45	75	10				
3:30			0.30	0.05	1.3	
4:00						Filter Filters very well.

Residue obtained 71 gr.

Assays on Residue, Zn - 29%, Co 1.03%, Cu 15.4%, Al 8.0%, Cd - "nil".

Cobalt held in Purif. Residue = $\frac{0.74}{41.4}$ = 1.8% available cobalt.

This purification shows that Fe can be oxidized in a filtered leach solution by air, provided ZnO is used in place of calcine; and, that leach solutions can be cleaned of Al if first separated from the leach pulp.

Cobalt was again occluded by the $Al(OH)_3$ precipitate.

In Purification #2 the ratio was 0.115 gr cobalt occluded per gr of Al precipitated.

In Purification #3 the ratio was 0.129 gr cobalt occluded per gr of Al precipitated.

Notice the amount of copper removed by the ZnO treatment.

Purification #7 and #8

Oxidize Fe in acid solution with $NaClO_3$.

Used commercial sodium chlorate screened thru 60 mesh, dissolved in water before adding to purification.

Use on #7) C.P. ZnO for basicity requirements.
" " #8) Zinc Plant melting furnace Dross, in place of ZnO.

Run on 1000 cc of Leach Solution #4 acidified to 1 gr H_2SO_4/Liter.

#7

Time	°C Temp	gr ZnO	gr $NaClO_3$	gr/L Fe	gr/L Al
9:10 A.M.	78			1.5	5.4
9:15			5		
9:30		10			
0:30	80			1.3	lower
:00		10			
:30 P.M.				nil	3.0

2:00 Filtered - slowly

#8

Time	°C Temp	Dross gr	$NaClO_3$ gr	gr/L Fe	gr/L Al
9:00 A.M.	70			1.5	5.4
9:05			5		
9:20		20			
10:50				1.3	lower
11:45	84	10			
2:00 P.M.				1:45	2.0

3:00 - Filtration impossible.
Add 10 gr Filter aid.
4:00 - Filtered - slowly

Iron can be oxidized with $NaClO_3$ in acid solution, and precipitated with ZnO.
Iron which has been oxidized cannot be precipitated with Dross.

This dross contains 10.7% metallic zinc, which acts as a reducing agent. These metallics are responsible for its inability to precipitate the iron as they not only continually reduce the iron to the ferrous state, but consume the added oxidizing agents.

Purification #9

This purification is based on the principle that $KMnO_4$ will oxidize Fe in basic solution, and that under favorable conditions, $KMnO_4$ will precipitate Mn as MnO_2.

Use 1000 cc leach solution #13 at 17.5 gr Co/L
$KMnO_4$ and C. P. ZnO.
$KMnO_4$ dissolved in water before adding.
ZnO emulsified with water before adding.

Time	Temp °C	$KMnO_4$ gr	ZnO gr	Fe gr/L	Mn gr/L	Al gr/L
8:40 A.M.	80			1.5	0.522	5.1
8:45		1.25				
8:50			20			
x 9:50						
10:00			5			
11:00				nil	0.740	low
11:05		0.50	5			
12:00 Noon					0.50	
12:30	70	0.26				
1:30					0.45	
2:15		0.24	3			
3:15	80				0.30	
3:45		0.16				
4:45					0.10	
5:30	Filtered; slow, but fast enough for plant operation.					

x Could not filter a sample.

47 gr Purification Residue at 2.03% Co and 32.0% Zn.

$\frac{0.955}{17.5} \cong$ 5.5% of available cobalt held in Purification Residue.

This purification demonstrates that Fe can readily be oxidized with $KMnO_4$ in basic solution and precipitated as the hydrate by ZnO. The reaction may be represented as follows:

$$6FeSO_4 + 2KMnO_4 + 5ZnO + 18H_2O \longrightarrow 6Fe(OH)_3 + 5ZnSO_4 + K_2SO_4 + 2MnO_2 + 9H_2O.$$

On this basis 1 gr Fe would require 0.947 gr $KMnO_4$ for oxidation.

The oxidation of manganous sulphate may be represented as

$$2KMnO_4 + 3MnSO_4 + 2ZnO + 2H_2O \longrightarrow K_2SO_4 + 5MnO_2 + 2ZnSO_4 + 2H_2O.$$

On this basis 1 gr Mn would require 1.92 gr $KMnO_4$ for oxidation.

The oxidation can be made preferential for Fe, as witnessed by the fact that all the Fe dropped out even though there was only enough $KMnO_4$ added to take care of about 90% theoretically. The higher Mn assay at 11:00 probably means that the solution was not basic enough for the formation of MnO_2 and that the $KMnO_4$ added went to $MnSO_4$. (This would explain the oxidation of Fe with less than calculated amount of reagent. The $KMnO_4$ has a higher oxidizing power in acid solution). With the addition of more ZnO manganese started to come out.

Purification #9 - continued

The oxidizer was purposely added in small increments in an attempt to titrate the manganese. Theoretically $KMnO_4$ requirements are:

(Fe) 1.5 x 0.947 = 1.42
(Mn) 0.522 x 1.92 = $\underline{1.00}$
2.42 Total $KMnO_4$.

When this amount had been added the purification was stopped.

The percentage of available cobalt (total Co in the solution.) held in the purification residue is disappointing.

Purification #10

Same principle as #9 but using zinc plant calcine in place of C.P. ZnO.

1000 cc of leach solution #14 at 17.3 gr Co/L.

Time	Temp °C	$KMnO_4$ gr	Calcine gr	Fe gr/L	Mn gr/L	Al gr/L
9:00 A.M.	80			1.5	0.522	5.1
9:05			75			
9:10		2.50				
10:30	75			nil	0.20	nil
10:40		0.40				
11:00					0.15	
11:10		0.30				
11:45					0.10	
12:00 Noon		0.20				
1:00 P.M.					0.10	

2:00 Filtered, slow but not impractical.

83 gr Purification Residue at 1.32% Co and 31.1% Zn.

$\frac{1.1}{17.3}$ = 6.4% of available cobalt held in Purif. Residue.

The theoretical quantity of $KMnO_4$ to satisfy both Fe and Mn requirements was added at one time. Notice that the 0.90 gr added in excess was inefficient, lowering the Mn only 100 mg, and that the cobalt loss in residue is rather high.

Purifications 11 & 12

Attempt to develop a purification technique using $KMnO_4$ and ZnO (or calcine) Use 1000 cc for each purif., from Leach No. 18, acidified to 2 gr H_2SO_4.

1. Make solution acid.
2. Add theoretical amount of $KMnO_4$ to oxidize Fe. (in acid solution.)
3. Add theoretical amount of ZnO for Fe and Al.
4. Agitate.
5. Add theoretical amount of ZnO plus 10% excess to take care of Mn.
6. "Titrate" manganese with $KMnO_4$ to precipitate MnO_2.

		#11					#12				
ime	°C Temp.	gr $KMnO_4$	gr ZnO	gr/L Fe	gr/L Mn	gr/L Al	gr $KMnO_4$	gr Calcine	gr/L Fe	gr/L Mn	gr/L Al
:45 A.M.	70			1.5	0.6	4.5			1.5	0.60	4.5
:50		0.85					0.85				
:00			23.7					39			
:45			1.2					2			
:00 Noon		1.2					1.2				
:00 P.M.	75			nil	0.30	low			nil	0.30	low
:10		1.1						9			
:30		0.6					0.6				
:00					0.22					0.22	
:15		0.5					0.5				
:00	74				0.20					0.20	
:00	Filtered very poorly						Filtered very poorly.				

Both attempts were fairly good purifications, but filtered very badly; too slow to be practical for plant operation. The technique is not successful. Notice that the manganese does not "Titrate" very well. As shown by #10, 11 & 12 the permanganate does not react stoichiometrically with the last 0.2 or 0.3 gr manganese in solution. It is being consumed by something else; probably precipitating Cobalt.

Purification #13

To be compared with #11 and #12.

1. Use 1000 cc leach solution #13 - not acidified.
2. Add theoritical amount $KMnO_4$ for Fe and Mn, in basic solution.
3. Add enough ZnO to cover total Fe, Mn & Al requirements
4. Observe filtration.
5. Add more $KMnO_4$ & ZnO if necessary.

Time	Temperature	$KMnO_4$	ZnO	gr/L Fe	gr/L Mn	gr/L Al	Filtration
9:00 A.M.	85			1.5	0.80	4.5	
9:05		2.7					
9:10			25				
10:20							Impossible - Could not filter a sample.
10:55			10				
11:45				nil	0.45	0.5	Fair-but not good enough. Could get sample.
12:40 P.M.		0.87					
12:45			5				
1:45				nil	0.38	very low	
2:30							Filtered very well.

This purification establishes the fact that a "theoretical" quantity of ZnO or $KMnO_4$ is insufficient for purification and filtration. It seem possible to obtain an excellent filtration, on a purification which in unfilterable, by merely adding ZnO in excess.

Perhaps a "one-addition" purification would be better. For example, if the whole of the ZnO had been added at one time, the efficiency of the $KMnO_4$, with respect to Mn might have been improved.

Purification No's. 14 & 15

Run on 1.5 liters of leach solution #24 at 45.2 gr Co/L. To be compared with #16.

14) Calcine only, to determine the amount of Co held in the Residue.
15 Calcine plus theoretical* requirement for Fe, only. *KMnO4
(Manganese not considered).

			14					15		
Time	Temp °C	Calcine gr	Fe gr/L	Mn gr/L	Al gr/L	$KMnO_4$ gr	Calcine gr	Fe gr/L	Mn gr/L	Al gr/L
8:00 A.M.	64		1.75	0.60	1.34			1.75	0.60	1.34
8:15						2.50				
8:20		30					27			
9:30	74		1.70	0.60	0.1			nil	0.60	0.4
10:00							3			
11:15								nil	0.60	0.1
12:00 Noon		Filtered well				Filtered well				

14: Obtained 27 gr Pur. Residue at 2.05% Co.

$\frac{0.56}{67.8}$ = 0.82% available Co held in Pur. Res.

15: Obtained 32 gr Pur. Residue at 1.76% Co.

$\frac{0.56}{67.8}$ = 0.82% available Co held in Pur. Res.

The comparatively low Al content of this solution (1.34 gr/L against the usual 4 or 5 gr/L) results in a residue which allows fast filtration.

The addition of $KMnO_4$ for Fe only does not seem to precipitate cobalt.

Purification #16

To be compared with #14 and #15. Use $KMnO_4$ and calcine. Run on 1.5 liters of leach solution #24.

Add $KMnO_4$ until Mn is below 100 mg/L - observe the effect of this excess $KMnO_4$ in regard to cobalt held in Purification Residue.

Time	Temp °C	$KMnO_4$ gr	Calcine gr	Fe gr/L	Mn gr/L	Al gr/L
12:00 Noon	75			1.75	0.600	1.34
12:15 P.M.			30			
12:20		2.6				
1:45				nil	0.744	0.1
2:15		3.0				
2:45				nil	0.524	0.1
3:15		3.4				
3:45					0.075	

4:15 Filtered well.

Obtained 37 gr Purif. Residue at 6.84% Co.

$\frac{2.53}{67.8}$ = 3.7% available Cobalt held in Purif. Residue.

The $KMnO_4$ added in an attempt to precipitate the manganese is responsible for the high cobalt loss in the residue.

With respect to Mn the $KMnO_4$ was very inefficient; for plant practice this procedure would be too expensive. To lower the Mn from 0.600 to 0.075 gr/L required 4.25 gr $KMnO_4$ per liter.

Purification No's 17 & 18

Use Sodium peroxide as oxidizer, plus ZnO.

#17) Make solution acid, add Na_2O_2, agitate, then sample. Add ZnO; try to precipitate manganese with Na_2O_2.

#18) Keep solution basic, add ZnO first, then Na_2O_2 to get Fe. Try to precipitate Mn with Na_2O_2.

Both run on 1.5 liters of leach solution #24. Add Na_2O_2 as dry powder.

	No.17							No. 18				
ime	Temp °C	acid gr/L	ZnO gr	Na_2O_2 gr	Fe gr/L	Mn gr/L	Al gr/L	ZnO gr	Na_2O_2 gr	Fe gr/L	Mn gr/L	Al gr/L
00	78	1			1.75	0.600	1.34			1.75	0.600	1.34
15				8.6				7.5				
30									8.6			
00	83				1.45	0.600	1.34			1.10	0.600	0.8
30		0	7.5					7.5				
15					0.55	0.60	0.8			0.15	0.600	0.1
00	80		7.5									
00					0.10	0.60	0.1					
00				1.3					1.3			
00						0.600					0.600	
45				1.0					1.0			
00						0.600					0.600	
30				1.0					1.0			
00	Filtered very well				nil	0.600		Filtered very well		nil	0.600	

Obtained 42 gr Pur. Res. at 4.94% Co

$\frac{2.07}{67.8}$ = 3.05% available Co held in Purification Residue.

Obtained 47 gr Pur. Res. at 4.66% Co

$\frac{2.19}{67.8}$ = 3.23% available cobalt held in Purification Residue.

Purifications #17 and #18 demonstrate that Fe can be oxidized by Na_2O_2, but that is not precipitated under these conditions.

The first addition of Na_2O_2 was purposely made about three times as large as the eoretical requirements for both Fe and Mn, as it was thought that Na_2O_2, being similar character to H_2O_2, might lose a considerable portion of its oxygen from the hot soluons as a gas. There was noticeable effervescence when the Na_2O_2 was added.

Na_2O_2 in water forms the system -

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2.$$

It was thought that the Na_2O_2 might supply enough basicity to precipitate the ron as hydrate or basic sulphate in #17, but this did not happen. A drop of only 300 mg/L as recorded. Upon the first addition of the ZnO the iron started coming out nicely and was inally cleaned from the solution.

A large excess of Na_2O_2 had no effect on the Mn in a definitely basic solution, seems to have precipitated some cobalt.

It seems likely that, if purifying for iron only, better efficiency on the Na_2O_2 ould be obtained by adding sufficient ZnO to care for the Aluminum at the start and then dding the required Na_2O_2.

Cobalt Oxide Production

Summary

Purification #19

To use Na_2O_2 as oxididant for Fe.
Then use H_2O_2 for precipitation of Mn. (3% solution)
ZnO for basicity.
Run on 1.5 L of leach solution #24 at 45.2 gr Co/L.

Time	°C Temp	gr ZnO	gr Na_2O_2	cc H_2O_2	gr/L Fe	gr/L Mn	gr/L Al
8:00	75				1.75	0.60	1.34
8:20		15					
8:30			8.7				
9:00	74	15					
10:00					0.050	0.60	0.1
10:30	65	3					
10:35				30			
11:15						0.60	
12:15				30			
1:30						0.60	
2:00		3					
2:05	60			30			
3:00						0.60	
3:30 Filtered very well						0.60	

obtained 54 gr Purif. Residue at 4.78 % Co.

$\frac{2.58}{67.8}$ - 3.8 % available Co held in Purif. Residue.

Hydrogen peroxide will not oxidize two valent manganese and precipitate it as MnO_2 under these conditions.

Sodium peroxide oxidizes the iron satisfactorily.

Purification # 21

This is the first large scale purification - run in a lead pot. Use 7000 cc leach solution #21 at 17.2 gr Co/L.

Use $KMnO_4$ and calcine.

Add calcine first, in one addition. (Sulphide sulphur = 0.3%)

Add $KMnO_4$ sufficient for Fe and Mn requirements plus a 75% excess.

Time	°C Temp	gr $KMnO_4$	gr Calcine	gr/L Fe	gr/L Mn	gr/L Al
9:00	45			1.10	0.500	5.3
9:30			600			
9:45		24.5				
10:30	53			nil	0.200	low
12:30	65					
1:00	65				0.200	
2:00	Filtered very well.					

Obtained 6850 cc Sol'n at 1.470 Sp. Gr.
740 gr Purif. Residue at ---- 1.37% Co
0.50% Cd
0.18% Cu
32.0 % Zn

gr Co in Residue 10.1 = 8.4% of available Co held in Purif. Residue.
gr Co available 121
in sol'n

Successful for filtration purposes.

This purification, like No's. 11, 12 and 13, shows that it is difficult, if not impossible, to precipitate the last few hundred milligrams of manganese, even with a substantial excess of $KMnO_4$.

The calcine used was chosen because of its low sulphide sulphur content in order to minimize the consumption of oxidizer.

The high loss of cobalt in the Purif. Residue again indicates that this element is being chemically precipitated as well as occluded; probably precipitated as a cobalt manganate by the permanganate.

Purification #24

Run on 7.5 litres of Leach Solution #24.

Used zinc plant calcine and $KMnO_4$
Used only enough $KMnO_4$ to oxidize iron in basic solution.

Oxidizer for manganese purposely omited.

Compare this large scale purification with P. No. 15.

Time	°C Temp.	gr Calcine	gr $KMnO_4$	gr/L Fe	gr/L Mn	gr/L Al
10:30	65			1.75	0.60	1.34
10:45			13.2			
11:00		150				
1:00	65			nil	0.60	nil

1:30 Filter
Obtained 8000 cc at 1.410 sp. gr. (including wash water)
Obtained 157 gr. Purification Residue at 1.2% Co.

$$\frac{\text{Gr Co in Residue}}{\text{Gr Co in 7.5 L Sol'n}} \quad \frac{1.88}{339} = 0.55\% \text{ of available Co held in Purif. Res.}$$

$$\frac{\text{Gr Co in Residue}}{\text{Gr Al precipitated}} \quad \frac{1.88}{10.1} = 0.186 \text{ gr Co precipitated per gr of Al.}$$

This purification confirms the results of P. No. 15. Notice the small amount of calcine (20 gr/L) necessary to clean the solution of aluminum.

Purification #25

This is another large scale purification run on 12.9 liters of leach solu-
on #25. To be compared with P. No. 21.

Used zinc plant calcine and $KMnO_4$.
Used only enough $KMnO_4$ to oxidize iron in basic solution. No attempt made to titrate manganese.

ime	Temp °C	$KMnO_4$ gr	Calcine gr	Fe gr/L	Mn gr/L	Al gr/L
0:00 A.M.	53			1.3	1.49	4.1
0:15			258			
0:20		17				
:30				nil	1.39	0.5
2:15 P.M.	68		26			
1:15						0.1

2:00 Filtered very well - obtained 12.0 liters of solution at 1.460 Sp. Gr. and
2.30 liters of wash water.

Obtained 325 gr Purif. Residue at 1.14% Co
9.8 % Cu
33.5 % Zn

$$\frac{\text{gr Co in Residue}}{\text{gr Co available in sol'n.}} \quad \frac{3.71}{560} = 0.66\% \text{ of available Co held in Purif. Residue.}$$

This was a very successful purification from the standpoint of oxidizer efficiency, filtration, and cobalt held in residue.

It is another indication that the $KMnO_4$ added for Mn precipitates cobalt. When the reagent is purposely left out, the cobalt held in the residue is only that which is occluded by the aluminum hydroxide. The $KMnO_4$ added for the Fe seems to have no effect on the cobalt.

The amount of copper removed by the calcine treatment is noteworthy.

Copper in 12.91 liters of solution at 5.75 gr/L = 74.2 gr.
" " 325 gr Purif. Residue at 9.8% Cu = 31.8 gr.

$$\frac{31.8}{74.2} = 43\% \text{ of copper in solution removed by calcine treatment.}$$

Purification #26

Run on 4.8 liter of leach solution #25. To be compared with P. No. 25. Use $KMnO_4$ and calcine.

In this case the $KMnO_4$ will be added in increments less than the theoretical iron requirements in an attempt to titrate the iron. No attempt made to oxidize the manganese.

Time	Temp ° C	Fe gr/L	Al gr/L	
8:35 A.M.	46	1.3	4.1	
8:40				Add 104 gr calcine
8:45				Add 3.20 gr $KMnO_4$ or 55% of the theoretical requirements for Fe.
9:45	60	0.40	0.5	
10:00				Add 1300 cc of evaporated wash water from P 25, having Fe content of 1.0 gr/L. P 26 now has volume of 6.1 liters at 1.5 gr Fe/
10:10				Add 29 gr calcine
10:15				add 2.60 gr $KMnO_4$, or 85% of the theoretical requirements for Fe
11:15	60	nil	0.1	
11:30				Filtered well. Obtained 6.45 liters of solution at 1.430 Sp. Gr. Obtained 130 gr Purif. Res. at 0.73% Co 8.3% Cu 31.0% Zn

$$\frac{\text{gr Cobalt in Purif Res.}\quad 0.95}{\text{gr Cobalt in Solution}\quad 217} = 0.44\%$$ of available cobalt held in Purif. Res.

Successful purification.

Disregarding the wash water added, the $KMnO_4$ requirements for the Fe in this purification were 5.8 gr. The only explanation offered for the excellent efficiency obtained from the oxidizer is that some of the Fe might have been ferric to start with. Notice the amount of cobalt held in the Purification Residue.

The copper removed in this case was 39% of all copper in solution.

Purification #40

The series 40 Purifications were run to obtain information as to the possibilities of treating a high copper leach solution, if such should be encountered in the plant.

The object is to eliminate the Cu and Al, and Fe if possible, without suffering an undue loss of Cd and Co.

The procedure will be to use metallic zinc to displace the Cu, and some form of zinc oxide (calcine) to precipitate the Al. No attempt made to remove iron.

Run on 2000 cc leach solution #40, kept acid during Cu precipitation.

Time	Temp °C	gr Zn dust	gr Calcine	gr Acid Added	Cu gr/L	Al gr/L	Fe gr/L
9:00 A.M.	39			1.45	8.5	5.2	2.0
9:15		2					
9:40				1.45			
9:45		2					
10:05				1.45			
10:10		2					
10:25				1.45			
10:30		2					
10:40		2					
10:50		2					
11:00				1.45			
11:05		2					
11:15					1.7		
11:45	43	1					
12:05 P.M.					1.0		
12:15		0.5					
1:15			120				
2:15	45					1.5	
2:45			40				
3:30						0.5	
3:45			20				
4:45						0.1	2.0

5:00 Filtered very well - obtained 2620 cc sol'n at 1.340 Sp. Gr. (including wash water).

obtained 190 gr Residue at	0.51% Co
	0.25% Cd
	9.0 % Cu
	23.0 % Zn

0.97 gr or 3.5% available Cobalt held in Purif. Residue.
0.47 gr or 2.0% available Cadmium held in Purif. Residue.

This purification demonstrates that it is possible to eliminate both Cu and Al without an excessive loss of Cd or Co, by carefully adding Zn dust to an acid solution. The cobalt precipitated, if considered to be entirely due to occlusion by $Al(OH)_3$, is in the ratio of .094 gr Co per gram of Al. (See Purification #3.)

Purification #41

To observe the effect of using zinc melting furnace dross for removal of Cu and Al.

This dross screened thru 60 mesh, contains 69% Zn as ZnO, and 81.2% total Zn. The metallic zinc content is about 11% or 12%. In this purification, the amount of dross added will be based on the removal of Al by the ZnO content. Any Cu, Cd and Co removed by the metallics will be co-incidental with this treatment.

Run on 2000 cc leach solution #40.

Time	Temp °C	Dross	Al gr/L	Cu gr/L	
10:00 A.M.	40		5.2	8.5	
10:15		100			
11:15	68		2.0	5.0	poor filtration
11:20		70			
12:30 P.M.	70		0.1	0.015	
1:15					good filtration. Vol. 2550 (including wash water). Sp. Gr. 1.326

Obtained 285 gr Residue at 1.25% Co
4.6 % Cd
6.0 % Cu
32.0 % Zn

3.56 gr or 13% available cobalt held in Purif. Residue.
13.1 gr or 60% " cadmium " " " "

This purification was successful for the removal of Al by ZnO in Dross but the loss of Co and Cd due to the metallic Zn was prohibitive. A better scheme would be to use the Dross to remove Cu and some Al, then finish the Al removal with calcine. (See Purification #42.)

Purification #42

To be compared with #41.

In this purification the copper will be removed by careful additions of zinc melting furnace dross so as to minimize the loss of Co and Cd by metallic precipitation. When the copper in solution is low enough, the remainder of the Al will be removed by additions of calcine.

Run on 1000 cc of leach solution #40.

Time	Temp $^{\circ}$C	Dross gr	Calcine gr	Cu gr/L	Al gr/L	
10:00 A.M.	66			8.5	5.2	
10:15		40				
11:15				1.2	high	filtered poorly
11:50		7				
12:30 P.M.				0.25	high	filtered poorly
1:15	70		50			
2:00					0.5	filtered better
2:15			20			
3:00					0.1	filtered well

Obtained 1680 cc sol'n at 1.324 Sp. Gr.
(including wash water)

Obtained 130 gr Purif. Residue at 1.0% Co
0.1% Cd
7.9% Cu
34.2% Zn

1.3 gr Co or 9.4% of available Cobalt held in Purification Residue.
0.13 gr Cd or 1.1% of available Cadmium held in Purification Residue.
Not a desirable purification.

The cadmium loss is not excessive but the Co loss is prohibitive. Evidently, the solution must be kept acid during the copper precipitation period if cobalt losses are to be avoided.

Purification #43

In this purification an attempt will be made to oxidize and precipitate iron with $KMnO_4$, after the Cu and Al have been removed similar to the procedure of P. 4C.

Run on 1000 cc of leach solution #40.

Time	Temp °C	Zn Dust gr	Acid gr	Calcine gr	$KMnO_4$ gr	Cu gr/L	Al gr/L	Fe gr/L
8:40 A.M.			0.3					
8:45	48	1				8.5	5.2	2.0
8:50		1						
9:00		1						
9:10	45	1	0.3					
9:15		1						
9:20		1	0.3					
9:25						3.4		
9:30		1	0.3					
9:35	41	1						
9:45			1.5					
10:00						0.8		
10:10	52	1	1.5					
10:30				60				
10:40	61				2.0			
11:00							1.0	1.2 *
11:15				20				
11:20					0.5			
12:00 Noon							0.3	1.0 Fair filtration
12:30 P.M.				10	1.0			
1:30								1.2 good filtration
2:00				10	1.0			
3:00								0.35
3:30					1.0			
4:30								0.35
5:30								0.35
6:00	Filtered well. Vol. = 1430 cc at 1.296 Sp. Gr. (including wash water)							

* Poor filtration.

Obtained 121 gr Purif. Residue at 0.7% Co (0.85 gr Co)
Not successful for removal of iron.
Theoretical requirements for iron are about 1.9 gr $KMnO_4$.

As it took 4.5 gr $KMnO_4$ to reduce the iron from 2.0 gr/L to 0.35 gr/L, it would seem that the metallic copper present in the pulp consumes most of the oxidizer, thereby preventing the $KMnO_4$ from oxidizing the Fe. The last gram of $KMnO_4$ had no effect whatsoever with respect to Fe.

Cobalt Oxide Production
Summary

Cadmium Sponging

As the utilization of the sponge cadmium was considered to be a problem in cadmium metallurgy, not much attention was paid to the process of removing the cadmium from the purified solution during this campaign. The usual prodedure was to assay for Cd, acidify to acid spot and add the calculated amount of zinc dust. If insufficient for complete cadmium removal the solution was again acidified and hit with zinc dust. No trouble was experienced in getting all the cadmium or in producing a floculent sponge.

The only element investigated in relation to the sponge was nickel. Invariably it was found that the zinc dust added for complete cadmium removal would precipitate only a portion of the nickel present. The barren solution (after the Co had been taken out by NaOCl) averaged between 1.5 to 2.5 gr Ni/L, and, if the Co had been dropped to below 1 gr/L, would have a green color. The Sponges averaged about 2.0% Ni. It should be pointed out that as copper or any other element precipitated by zinc dust will find its way into the sponge it is desirable to eliminate such elements either in the leaching or purification process.

Cobalt Oxide
Production

COBALT OXIDE PRODUCTION

The recovery of cobalt from the purified sulphate solutions is based on the principle that alkaline sodium hypochlorite will precipitate cobalt as $CO(OH)_3$. The reaction might be represented as follows:

(1) $2CoSO_4 + NaOCl + 4NaOH + 3H_2O \longrightarrow 2Co(OH)_3 + 2Na_2SO_4 + NaCl + 5H_2O$

Although this equation gives a picture of the reaction, and truthfully shows that 1 gram molecular weight of hypochlorite will precipitate 2 gr. mol. wt. of cobalt, it does not adequately show the chlorine or the caustic requirements for the cobalt. In order to explain all the factors involved it is best to start with the manufacture of the reagent.

The reagent is prepared by bubbling dry chlorine gas into a cool solution of sodium hydroxide. The chlorine gas and the caustic react according to the equation $2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$. (2) Thus, for every molecule of NaOCl formed, there is formed one molecule of water and one molecule of NaCl which, although inert, nevertheless consumes chlorine. If equation (1) were to be used without accounting for this inert salt in the hypochlorite a serious error would be made in calculating the theoretical chlorine requirements for cobalt. When the inert chlorine is included in the total it will be seen that, stoichiometrically, 70.91 gr Cl_2 are required for every 117.88 gr Cobalt, if sodium hypochlorite is used as the precipitant. This same relationship between Cl_2 & Co may be arrived at by considering the problem from the standpoint of oxidation.

(3) $2CoCl_2 + Cl_2 \longrightarrow 2CoCl_3$. (Here the chloride radical is used, instead of the sulphate, for simplicity).

According to equation (2) it will be seen that 40.0 gr of NaOH are required to react with 35.45 gr chlorine. This means that 2 gr molecular weights of caustic are required for every gram mol. wt. of hypochlorite or at least 1.13 gr of NaOH must be present in solution for every gram of Cl_2 that is expected to be dissolved; otherwise some chlorine will escape into the air and be wasted. For purposes of cobalt precipitation there is always an amount of caustic present which so exceeds the theoretical requirements for chlorine that if simple precautions are taken, practically no chlorine is lost in manufacturing the hypochlorite.

The caustic requirements for cobalt precipitation may be considered as follows: In equation (1) it appears that two gram molecular weights of caustic are required for every gram mol, wt, of Cobalt. However, one-half gram molecular weight of hypochlorite is also required and as equation (2) shows that 2 gram moles of caustic are necessary to make 1 gram mole of hypo, it therefore becomes evident that to completely satisfy the cobalt requires a total of three gram moles of caustic. This relationship between the caustic and cobalt may be determined in a more simple manner by considering the (OH) ion requirements. It is known that the cobalt precipitate is mostly $Co(OH)_3$, therefore three NaOH molecules will be necessary to supply the three (OH) ions for one molecule of cobalt.

Thus, in the precipitation data presented with this investigation an hypochlorite solution containing chlorine and caustic in the ratio of 1/2 gr. mol. wt. Cl_2 to 3 gr. mol. wt. NaOH is taken as the standard, as that is the solution which will theoretically precipitate 1 gr. mol. wt. of cobalt. A solution containing 240 gr NaOH per litre and 70.91 gr Cl_2 per litre was found to be a satisfactory standard concentration.

By "excess" chlorine in the hypochlorite is meant the amount of chlorine over that which is necessary to produce the gr. mol. wt. ratio 1 Cl_2 to 3 NaOH. For example a 40% excess chlorine solution, in the case of the practical standard given above, would be 240 gr NaOH/l and 100 gr Cl_2/L (99.27 exact). The excess is 40% of 70.91, added to the standard concentration. The reason for the excess chlorine is to hold the zinc in solution so that the zinc content of the cobalt oxide product will be within reasonable limits. In precipitating cobalt with hypochlorite it is absolutely necessary to add the caustic requirements simultaneously with the chlorine, otherwise the chlorine escapes from solution unused. It is fundamental to have the (OH) ions available at the same time the cobalt is oxidized in order to obtain a precipitate of $Co(OH)_3$. In a pure solution of $CoSO_4$, the precipitation proceeds in an orderly manner when using the standard solution previously described (71 gr Cl/L and 240 gr NaOH/L). Unfortunately, the presence of zinc, especially in a concentration from four to ten times the concentration of the cobalt, complicates matters by entering into a side reaction with the caustic:

$$2Na(OH) + ZnSO_4 \longrightarrow Zn(OH)_2 + Na_2SO_4$$

Unless this zinc hydrate is decomposed with an acid it finds its way into the final product, sometimes in very substantial amounts. The easiest way to maintain an acid condition in the solution is to introduce "excess" chlorine, along with the hypochlorite. For purposes of illustration, let it be assumed that 1 cc of hypochlorite containing 100 mg Cl_2 and 240 mg NaOH are added to a zinc sulphate, cobalt sulphate solution. Stoichoimetrically 71 mg of Cl_2 and 240 mg Na(OH) should be used in precipitating 117.88 mg Co, while 29 mg of Cl_2 are set free. A portion of the free chlorine dissolves to form HCl, thereby creating an acid condition and tending to prevent the formation of $Zn(OH)_2$.

During this investigation it was found impossible to completely prevent the zinc from entering the final product, even when large excesses of chlorine were tried. There is a practical limit to the amount of chlorine that can be added because of the human factor. The high excess chlorine hypochlorites liberate so much chlorine during the precipitation process as to create hazardous working conditions. A hypo solution containing as high as 40% excess chlorine, however, can be used with perfect safety and without creating a disagreeable atmosphere, provided it is added to the cool solutions (25-40°C) and at a reasonably slow rate.

It was found that even when calculated on the caustic basis, a theoretical amount of hypochlorite was never sufficient to completely precipitate all the cobalt. For practical purposes an additional amount of 10% to 20% of hypo was usually necessary to get the cobalt down to an acceptable range before filtration (about 0.5 gr Co/L). This is accountable by the two facts that the hypochlorite is not 100% efficient due to the zinc consuming (OH) ions, and that all the manganese is precipitated as MnO_2 by the hypo. Any traces of iron or aluminum are also precipitated by the hypo.

The maximum percentage of Cobalt in pure $Co(OH)_3$ is 53.7%. During this investigation some uncalcined $Co(OH)_3$ material was found to run as high as 54% Co even when zinc, iron and manganese were present as additional impurities. This was due to the drying period, at 110°C, previous to assaying, which caused some of the hydrate to decompose, giving the higher cobalt assays. The material is designated as $Co(OH)_3$ in order to distinguish it from cobalt oxide (Co_3O_4) which can be prepared from the precipitate by calcining it as 750-800°C. Calcining a material of 50%-53% to obtain a 60 to 65% cobalt content was not uncommon.

The impurities in the $Co(OH)_3$ product will be zinc, iron, manganese, chlorine & sulphur. No antimony, arsenic, nickel or calcium, even in traces, was found. It is interesting to note that consumers of cobalt oxide or firms which buy cobalt bearing material for reworking, consider chlorine, sulphur, iron and calcium to be the most undesirable impurities. The iron in this product is as low as that which is usually found in high-grade commercial cobalt oxide, while chlorine can be kept down to the range of 0.5% or lower merely by washing the precipitate thoroughly, in the press, with cold water. The sulphur in the $Co(OH)_3$ frequently runs as high as 2.6% but this can be removed by calcining the material at a temperature slightly higher than the decomposition temperature of zinc sulphate. On one sample a calcination at 750°C for 1/2 hour reduced the sulphur from 2.6% to 0.26%. Consumers were unanimous in stating that zinc in very substantial amounts could be tolerated - one said as high as 10% Zn. The reason given was that zinc is a non-chromogenic material and the only effect it would have would be to dilute the cobalt oxide.

Cobalt Oxide Production

Precipitation #1

Run on 2900 cc of Leach Sol'n #8, unpurified.

To determine the need, if any, for purification of solution before precipitation of cobalt.

Sodium Hypochlorite used contained 115 gr Cl_2/L and 300 gr NaOH/L.
(a 30% excess chlorine solution.)

Time	Temp °C	Co gr/L	NaOCl cc	
8:45 A.M.	40	15.0		Added NaOCl very slowly
10:20			440	Maintained a slightly acid condition due to excess Cl_2.
				Brown precipitate observed. Very persistant light froth.
10:30		2.0		Poor filtration
10:45	35		110	This amount represents a total of 25% over the theoretical hypo for 100% cobalt precipitation.
10:50		0.5		Solution went neutral or basic.
11:10				Filtration practically impossible 100cc thru filter in 3 hrs.

$Co(OH)_3$ product: Estimated 140 gr should be obtained.
Actual assays of product,

Co --- 30.4%
Zn --- 6.9%
Fe --- 2.1%
Mn --- 0.45%
Al --- 7.4%
Ni --- nil

The need for purification is clearly demonstrated in this precipitation. First, the final product is undesirable from the standpoint of buyers of cobalt oxide because of its high impurity and low cobalt content. Secondly, the presence of Aluminum results in the formation of $Al(OH)_3$ making the precipitate impossible to filter on a plant operation basis.

The removal of Fe or Mn is a question of economics but the purification of the solutions to eliminate aluminum is absolutely essential if the process is to be practical.

Cobalt Oxide Production

Precipitation No's 2 and 3

Each Run on 500 cc of Leach Solution #12 unpurified.

Use hypochlorite containing 43.4 gr Cl/L and 120 gr NaOH/L.
(a 22% excess chlorine solution)

#2 at 80 C to 85°C. #3 at 40°C.

	#2			#3			
Time	Temp	Hypo cc	Co gr/L	Temp	Hypo cc	Co gr/L	
12:15 P.M.	60		19.8	40		19.8	
12:45	85	136		40	136		Add hypo slowly
2:00			3.5			2.5	
2:10		13			13		
2:45			2.4			1.8	
3:00		14			14		
3:20	80		2.2	40		1.1	
3:30	Very difficult to filter			Very difficult to filter			

Obtained 19.0 gr $Co(OH)_3$ product	Obtained 15.6 gr $Co(OH)_3$ product
at 36 % Co	at 38.2% Co
2.8% Zn	2.5% Zn
6.3% Fe	7.0% Fe
1.34% Mn	1.49% Mn
2.7% Al	1.5% Al
0.0% Ni	0.0% Ni
0.6% Sb	0.8% Sb

This confirms the results obtained in #1; product is low in Cobalt, high in impurities and filtration is impractical, even at high temperatures.

The low temperature precipitation seems to give a little better efficiency of the hypochlorite, as would be expected due to the better retention of chlorine in a lower temperature solution.

A more dilute solution of hypochlorite than that used in #1 did not improve the purity of the final product, appreciably. An excess of 20% over the theoretical required for complete cobalt precipitation instead of 25%, plus the fact that this excess was added more slowly than in #1 might account for the low zinc and aluminum content of the product. The amount of cobalt left in solution would be uneconomic in plant practice.

Cobalt Oxide Production

Precipitation No's 4 and 5

Each run on 1000 cc of Leach Solution #13 purified of Fe and Al with $KMnO_4$ and calcine.

Use hypochlorite containing only 13% excess chlorine; 80 gr Cl_2/L and 240 gr NaOH/L.

To compare relative efficiency of hypochlorite when used in acid or basic sol'n.

To compare final product with those obtained in No's 1, 2 and 3.

		#4				#5		
Time	° Temp	hypo cc	gr/L Co	Acidity	° Temp	Hypo	gr/L Co	Acidity
10:00 A.M.	70		14.1	Acid Spot	70		14.1	3 gr NaOH
10:15		111				111		
11:30	68		3.6	Acid Spot	80		3.0	basic spot
11:45		30				28		
1:00 P.M.			1.2	Neutral Spot			0.8	Basic spot
1:45		5						
2:00				Neutral Spot				Add 1.5 gr H_2SO_4
2:20			1.0	Add 1 gr H_2SO_4				
3:15	Filtered well				Filtered Wall			Acid Spot

146 cc Hypo to precipitate 13.1 gr Co,
0.898 gr Co per cc NaOCl

Obtained 24 gr $Co(OH)_3$ at
49.9 % Co
8.8 % Zn
1.1 % Mn
tr Fe
nil Ni
nil Al

139 cc Hypo to precipitate 13.3 gr Co
0.945 gr Co per cc NaOCl

Obtained 25 gr $Co(OH)_3$ at
47.9 % Co.
10.8 % Zn
1.2% Mn
tr Fe
nil Ni
nil Al

Precipitation of cobalt from a basic solution results in a slightly better efficiency of the hypochlorite but raises the zinc content of the final product. There is not enough saving made in reagent to favor a basic precipitation.

A direct comparison of #4 to Nos 1, 2 and 3 show that it is possible to make a cobalt product approaching and perhaps surpassing 50% Co content, with good filterability, if the leach solutions are first purified of Al and Fe.

The high zinc content of the final product could, perhaps, be lowered if a hypochlorite containing a greater excess of chlorine were used so as to keep the solution acid all the time.

Summary

Cobalt Oxide Production

Precipitation #6

Run on 1070 cc of Leach Solution #14, Purified with $KMnO_4$ & calcine.

Use hypochlorite containing 27% excess chlorine; 90 gr Cl_2/L and 240 gr NaOH/L.

Keep solution acid by additions of small amounts of dilute H_2SO_4 whenever necessary.

Compare product with #4.

Time	°C Temp	cc Hypo	Co gr/L	Acidity	
11:30 A.M.	60		14.7	acid spot	
11:45		30	high	" "	
1:00 P.M.		30	lower	" "	
2:00		30	"	" "	
2:30		15			105 cc Hypo represents the theoretical weight of Cl_2 for complete cobalt precipitation (Still deficient in caustic)
3:00		11	"	" "	
3:15		6	"	" "	
3:30		5	"	" "	
3:40		5	"	" "	
3:50		5	"	" "	135 cc hypo represents the theoreticalweight of caustic necessary to supply the OH ions for complete cobalt precipitation.
4:00			1.5	" "	

4:15 Filtered well

Obtained 1210 cc barren solution at 1.390 Sp. Gr.

23.0 gr Co $(OH)_3$ at 54 % Co
5.35% Zn
0.09% Mn
0.07% Fe
0.0 % Ni
0.0 % Al
0.0 % Sb

Very little acid was used to keep this precipitation on the acid side. The higher the excess chlorine in the hypochlorite the less tendency for the solution to go basic. Perhaps a 40% excess chlorine hypo might keep the precipitation acid without any aid from dilute H_2SO_4.

Precipitation on the acid side seems to yield a much more marketable product.

The 1.5 gr Co/L left in the solution was done purposely to see if a zinc-free product could be obtained. Evidently it is impossible, by the use of sodium hypochlorite to precipitate cobalt from a solution in which the zinc concentration is from six to ten times the cobalt concentration, without co-precipitating some of the zinc.

Cobalt Oxide Production

Precipitation No's 7 and 8

Duplicate precipitations run on 1000 cc of leach solution #15 purified with $KMnO_4$ and calcine.

#7 differs from #8 only in the rate of adding hypo.

Sodium hypochlorite used contains 70% excess chlorine
120 gr Cl_2/L and 240 gr NaOH/L.

#7

Time	°C Temp	cc Hypo	gr/L Co
10:00 A.M.	40		15.0
10:15		50	
10:40	48	28	
11:30	56		
12:00 Noon		15	high
1:00	64	15	
1:30	55	10	
2:00			0.9
2:15		10	
2:30			0.7
3:00		5	
3:15			0.5

4:00 Filtered well
20.0 gr $Co(OH)_3$ at 53.5% Co and 3.9% Zn.

#8

cc Hypo	Co gr/L
	150
50	
50	
28	
	0.6
Filtered well	

20.5 gr $Co(OH)_3$ at 52.5 % Co and 4.5% Zn.

These precipitations show that, even with 70% excess chlorine in the hypochlorite, which keeps the solution acid all the time, it is impossible to get a zinc-free product. Precipitations of this type would be impractical in the plant because of their disagreeable character. When this 70% excess chlorine is added to the purified solution so much chlorine is liberated as to make the surrounding atmosphere unbearable.

The additions of hypochlorite to #8 were stopped at 128 cc as this amount contains the theoretical caustic requirements for complete cobalt precipitation. In 128 cc of hypo were 15.3 gr Cl_2 or 66% more than the theoretical requirement for Co.

Cobalt Oxide Production

Precipitation Nos. 9 & 10

Object: To observe the effect of NaOCL containing very little excess chlorine.

#9) Use hypochlorite containing 10% excess chlorine (78 gr Cl_2/L (240 gr NaOH/L

#10) Use hypochlorite containing 20% excess chlorine (85 gr Cl_2/L (240 gr NaOH/L

Both run on 2 L of combined Purifications of leach 24 at 40°C (During manipulation and storage the original solution has been concentrated about 12%)

#9

ime	cc Hypo	gr/L Co	Acidity
2:30		52.1	Basic Spot
2:45 to 1:15	885		Basic Spot
1:45		lower	Basic Spot
2:00	180		
2:15		lower	Basic Spot
2:30	180		
2:40		lower	Basic Spot
2:45	90		
3:00		lower	Basic Spot
3:10	45		
3:20		lower	Basic Spot
3:30	30		
3:40		0.3	

3:50 Filtered-Sol'n at 43.0 gr/L
Obtained 280 gr $Co(OH)_3$ at 33% Co
19.5% Zn
0.6 Mn
tr Fe

Used 59% excess NaOCl
Total reagent used contained a 59% NaOH excess and a 75% Cl_2 excess

#10

Time	cc Hypo	gr/L Co	Acidity
12:02		52.1	Basic Spot
12:10 to 12:35	885		
1:00		lower	Basic Spot
1:30	180		
2:10		lower	Basic Spot
2:20	180		
2:35		lower	Basic Spot
2:50	90		
3:05		lower	Basic Spot
3:15	45		
3:25		0.3	Basic Spot

3:30 Filtered-Sol'n at 53.0 gr Zn/L
Obtained 262 gr $Co(OH)_3$ at 39.6% Co.
14.0% Zn
0.7[illegible] Mn
5tr Fe

Used 56% excess NaOCl
Total reagent used contained a 56% NaOH excess and a 87% Cl_2 excess

These precipitations show that neither a 10% or 20% excess chlorine solution of aOCl will keep the precipitation acid or cause it to become acid. They will not yield good $Co(OH)_3$ product, even on a purified solution.

No. 10 might be compared to Prec. No. 5 which gave a good end product. The igher zinc in Prec. No. 10 was due to the fact that it was basic throughout, that it was ot reacidified before filtration, the cobalt in solution was brought lower, and a much reater amount of NaOCl per litre was used then in No. 5. (690 cc/L against 139 cc).

Precipitation Nos. 9 & 10 (Cont)

At this point attention should be called to the fact that this precipitation acted differently than any heretofore. The high concentration of Co (52.1 gr/L or roughly 3 times the usual amount) resulted in a precipitate best described as "nodular". Whereas the lower concentration of Co (15-20 gr/L) gave a soft precipitate which would agitate in the solution, this high cobalt solution gave a precipitate which would float on top, and by attaching itself to the walls of the vessel, remain stationery while the solution revolved beneath it. It contained small nodules, probably $Zn(OH)_2$ relatively hard in texture. It was coherent or tenacious enough to support itself and would build up as the reagent was added. It had to be pushed back into solution with a stirring rod.

Cobalt Oxide Production

Precipitation #11

Object: To compare with Precipitation Nos. 9 & 10.

Use NaOCl containing 40% excess chlorine – (100 gr Cl/L
(240 gr NaOH/L

Run on 2 L of combined purified solution #94 – acidified to acid spot before first addition of hypo.

Time	°F Temp	cc Hypo	gr/L Co	Acidity
8:30	58		52.11	Acid Spot
9:00 to 10		885		
10:00				Acid Spot
10:20		90		Acid Spot
10:40	50		2.0	
10:45		90		Acid Spot
11:15	45		1.4	Acid Spot
11:30		45		
12:00	40		0.4	Acid Spot

1:00 Filtered – solution at 79 gr Zn/L
Obtained 182 gr $Co(OH)_3$ at 51.0% Co.
5.1% Zn
1.0% Mn
tr Fe
nil Ni

Used 25% excess NaOCl.
Total reagent used contained a 25% NaOH excess and a 79% Cl_2 excess.

NaOCl containing 40% excess chlorine will keep the precipitation acid all the time and will yield a good $Co(OH)_3$ product. There is a definite saving in caustic where a high chlorine NaOCl is used. If added slowly a 40% excess chlorine NaOCl does not liberate enough chlorine from the precipitation to be disagreeable.

The "nodular" precipitate was again observed but did not build up to same extent as in Nos. 9 & 10 nor did the particles seen so hard.

Cobalt Oxide Production

Precipitation Nos. 12 & 13

Object: To observe the effect of using a more concentrated NaOCl.

Contains 125 gr Cl_2/L and 300 gr NaOH/L
(a 40% excess chlorine solution)

#12) High temperature at start-Run on 2 L of Purif. 24.
#13) Low temperature throughout-Run on 1 L of Purif. 24.
Both precipitations made acid at start.

#12

Time	°C Temp	cc Hypo	gr/L Co	Acidity
10:00	75		52.1	Acid Spot
10:15 to 10:55		700		
11:00				Basic Spot
11:20	70	140		
11:45			4.0	"
11:50	58	70		
12:45			1.0	"
12:50	45	35		
1:00			0.5	"

1:50 Filtered-Solution at 75.0 gr Zn/L

Obtained 122 gr $Co(OH)_3$ at 46.4 % Co
9.5 % Zn
0.9 % Mn
tr Fe
nil Ni

25% excess NaOCl used.
Total reagent used contained a 25%
NaOH excess and a 77% Cl_2 excess.

#13

Time	°C Temp	cc Hypo	gr/L	Acidity
1:00	27		52.1	Acid Spot
1:15 to 2:20		550		
2:30				Acid Spot
2:45		70		
3:00			5.0	"
3:10		35		
3:30			1.5	"
3:40		17		
4:00	27		0.3	"

4:15 Filtered-Solution at 81.0 gr Zn/L

Obtained 88 gr $Co(OH)_3$ at 52.5 % Co
4.0 % Zn
0.95% Mn
tr Fe
nil Ni

25% excess NaOCl used.
Total reagent used contained a 25%
NaOH excess and a 77% Cl_2 excess.

#12 was so hot at the start that it liberated enough chlorine to make the vicinity of the precipitation untenable. Notice that the precipitation went basic at 11:00 A.M. The loss of chlorine is reflected in the relatively poor $Co(OH)_3$ product.

#13 was very successful. Evidently a solution containing as high as 500 gr NaOH/L can be used if the precipitation is performed in the cold, and the NaOCl added slowly.

"Nodular" precipitate again observed.

Cobalt Oxide Production

Precipitation #14

Run on 10500 cc of purified solution from Leach #30, in a lead lined agitator.

Used sodium hypochlorite containing 100 gr Cl_2/L and 240 gr NaOH/L (a 40% excess chlorine solution)

Object: To observe the relationship between cobalt and zinc in the final product, as the cobalt is precipitated from solution.

Time	°C Temp	cc Hypo	Acidity	gr/L Co	$Co(OH)_2$ Product % Co	 Zn	REMARKS
9:30	53		Basic Spot	24.3			
9:30		500	"				
10:00	61	500	"				
10:30		400	"				
11:00	63	300	"				
11:30		200	Acid Spot				
12:00	60	200	"				
12:30		70	"				
1:00	49			4.1	53.4	3.2	2170 cc represent the theoretical hypo requirements for complete Co precipitation.
1:20		210	Acid				
1:45	47			2.9	52.8	5.3	
1:55		210	"				
2:15	45			1.5	52.6	6.8	
2:25		210	"				
2:45	45			0.6	52.0	7.7	
2:55		105	"				
3:15				0.2	49.0	9.8	2905 cc represent 34% excess hypochlorite over theoretical.

3:30 Filtered well

This precipitation demonstrates that a high grade cobalt oxide product could be made if the precipitation were stopped considerably short of complete cobalt removal.

The final additions of hypochlorite to get the last few grams of cobalt are very inefficient - only 56% so. The first 2170 cc were 83% efficient. Both efficiencies figured on a caustic basis of 2.04 gr NaOH per gram of Co.

This precipitation was run too hot during the initial addition of NaOCl. Had it been performed at 40°C or lower the first 2170 cc would have dropped the cobalt to under 3 gr/L.

No trouble was encountered with a "nodular" precipitate such as in Prec. Nos. 8 to 13.

Cobalt Oxide Production

Precipitation No. 15

Run on 9.6 litres of Purif. No. 25, unacidified at start.

Routine precipitation with NaOCl containing 100 gr Cl_2/L and 240 gr NaOH/L. (a 40% excess chlorine solution)

Used commercial caustic to make NaOCl.

Time	°C Temp	cc Hypo	gr/L Co	Acidity
11:30	30		40.0	Basic Spot
1:45 to 2:00		1700		
2:15	33			Acid Spot
2:15 to 3:00		900		
3:05			6.0	Acid Spot
3:10 to 3:20	39	260		
3:25			3.0	Acid Spot
3:25 to 3:30		130		
3:40			2.0	Acid Spot
3:40 to 3:45		130		
3:55	38		1.4	Acid Spot
4:00 to 4:05		130		
4:20	35		0.8	Acid Spot

4:50 Filtered well

Obtained 12700 cc at 1.340 sp. gr. Zn @ 102 gr/L

Obtained 686 gr $Co(OH)_3$ at 50.8% Co
4.0% Zn
2.38% Mn
0.05% Fe
nil Ni

The high Mn in the final product was due to the leach (#25) having been run with zinc plant electrolyte unstead of C. P. H_2SO_4.

The commercial caustic makes a clear hypochlorite having a slightly darker color than that made with C. P. NaOH.

"Nodular" precipitate again observed but no so coherent as is Prec. Nos. 9, 10 & 11. Dropped back into solution on agitation.

Cobalt Oxide Production

Precipitation # 21

Large scale precipitation run on 6850 cc of Purification #21, in a lead-lined agitator.

Use hypochlorite containing 40% excess chlorine
100 gr Cl_2/L and 240 gr NaOH/L.

Time	°C Temp	cc Hypo	gr/L Co	Acidity
8:45 A.M.	45		15.4	Acid spot
9:00		500		" "
9:30		200		" "
10:00		100		" "
10:20		50		" "
10:45	45		3.0	" "
11:00		50		
11:10			2.7	" "
11:15		50		
11:30			2.0	" "
11:45		25		
12:45 P.M.			1.7	" "
1:00	45	25		
1:15			1.2	" "
1:30		25		
2:00		25		
3:00			0.8	" "
3:30	Filtered well			

900 cc hypo represents the theoretical caustic requirements for complete cobalt precipitation.

Total hypo added represents a 14% NaOH excess and a 69% chlorine excess.

Obtained 6950 cc Sol'n at 1.420 Sp. Gr. ← Zn = 165 gr./L
Obtained 175 gr $Co(OH)_3$ at 53.0 % Co
5.0 % Zn
0.37% Mn
0.10% Fe

A 40% excess chlorine hypochlorite keeps the solution acid, does not liberate enough chlorine to make conditions disagreeable, and gives a reasonably high-grade cobalt oxide product.

Cobalt Oxide Production

Precipitation Nos. 40 and 41.

Run on Purified Solution #40 to determine the grade of cobalt oxide product obtained when the solutions are not purified for Fe or Mn.
1200 cc at 1.9 gr Fe/L, 0.52 gr Mn/L and 10.4 gr Co/L.

#40) Use a 30% excess chlorine NaOCl, 115 gr Cl_2/L and 300 gr NaOH/L
#41) Use a 40% excess chlorine NaOCl, 125 gr Cl_2/L and 300 gr NaOH/L

#40

Time	°C Temp	cc Hypo	gr/L Co	Acidity
10:00	40		10.4	Acid Spot
10:00 to 11:50		108		
12:00			2.5	" "
12:15 to 12:30		10		
1:00			1.3	Neutral Spot
1:15 to 1:20	40	10		
2:10			0.6	Basic Spot
2:20	Filtered well			

$Co(OH)_3$ 42.8 % Co
6.8 % Zn
7.1 % Fe
1.5 % Mn

#41

Time	°C Temp	cc Hypo	gr/L Co	Acidity
9:30	40		10.4	Acid Spo
9:30 to 11:45		108		
11:50			1.2	" "
12:00 to 12:15		10		
1:00			0.8	" "
1:00 to 1:15		10		
2:00			0.3	" "
2:20	Filtered well			

$Co(OH)_3$ 45.0 % Co
5.8 % Zn
7.1 % Fe
1.6 % Mn

In both cases the NaOCl used was 51% in excess of the theoretical cobalt requirements, instead of the usual 20% or 25%. The difference represents the amount of NaOCl consumed by the Fe and Mn.

Co(OH)$_3$ Retreatment

This short investigation was undertaken in an attempt to show in what form the zinc occured in the Co(OH)$_3$, and the possibilities for removing same from the product if it ever became advantageous to do so.

The re-treatment consisted of agitating some wet Co(OH)$_3$ (about 50% moisture) just as it came from the suction filter funnel, in 500 cc of different strength solutions containing ammonium hydroxide plus ammonium chloride.

No.	gr. Wet Co(OH)$_3$	Co(OH)$_3$ before Treatment % Co	% Zn	500 cc Sol'n gr/L NH$_4$OH	gr/L NH$_4$Cl	Co(OH)$_3$ after Treatment $ Co	% Zn	Dissolved Co-grams	Temp °C
A	100	49.0	5.7	10	20	50.2	4.2	0.1	30
B	100	49.0	5.7	50	50	55.0	1.7	2.6	60
C	100	49.0	5.7	100	100	56.8	0.4	115	30

These re-treatments show that the zinc is present as Zn(OH)$_2$ or as basic zinc sulphate, as it is soluble in NH$_4$OH - NH$_4$Cl solutions.

Not much cobalt is dissolved if the retreatment is carried out at room temperature.

Obviously it would be uneconomic to leach with a solution such as was used in C, especially if the solution were discarded after one leach. However, if purchasers of the product made it attractive enough to eliminate the zinc, some scheme involving the repeated use of the same solution, until saturated, might be investigated.

Production of Rinmann's Green

This investigation was undertaken in an effort to provide a possible outlet for both zinc and cobalt, should an overproduction of zinc sulphate solution result from retreating the cobalt residue. It is shown here that a paint pigment could be manufactured from our solutions without involving much manipulation.

Rinmann's green in a solid solution of cobalt zincate in zinc oxide; corresponding the formula $ZnO \times CoZnO_2$, depending on how much cobalt is present. In this case it is produced by co-precipitating with sodium carbonate, basic zinc sub carbonate and basic cobaltous carbonate from the zinc and cobaltous sulphate solution according to the reactions:

$$5ZnSO_4 + 5Na_2CO_3 + 4H_2O \text{ ---- } (5ZnO \cdot 2CO_2 \cdot 4H_2O) + 5Na_2SO_4 + 3CO_2$$
$$5CoSO_4 + 5Na_2CO_3 + 4H_2O \text{ ---- } (5CoO \cdot 2CO_2 \cdot 4H_2O) + 5Na_2SO_4 + 3CO_2$$

These co-precipitated carbonates are filtered, washed and dried. This product, which has a pale rose color, is subjected to calcination at 750°C for 1/2 hour during which process it loses both H_2O and CO_2; the zinc going to ZnO and the cobalt to CoO. This final mixture is a definite green, the exact shade of which depends upon the amount of cobalt present in relation to the zinc.

Rinmann's Green Production
No. 1

This preliminary precipitation was run to determine a Zn - Co ratio which would yield an acceptable green color upon calcination of the carbonates.

The procedure was to subject 2000 cc of Purified solution to the action of fixed amounts of NaOCl. Samples of solution were taken at each stage during the cobalt drop, and these samples were then treated with sodium carbonate to produce the raw pigment material. After calcination the color of each Zn - Co ratio was recorded.

No.	Pigment analysis		Color
	% Co	% Zn	
1	9.7	52.0	Green with gray black.
2	7.8	52.6	dull dark green.
3	7.5	52.9	good looking dark green.
4	7.4	59.5	dull dark green.
5	7.1	60.1	" " "
6	6.8	61.0	" " "
7	6.5	61.5	" " "
8	6.3	63.5	" " "
9	5.2	63.8	brilliant light green.
10	4.3	68.8	lighter Green.
11	2.8	69.0	very faint green.
12	0.3	69.7	incipient green.

The one chosen as the most attractive was #9 which has a Zn - Co ratio of 12 to 1 by weight.

Rinmann's Green Production
No. 2

A purified solution was subjected to NaOCl until the Cobalt was 8.1 gr/L. At this point the Zinc was 90.0 gr/L. Enough purified $ZnSO_4$ from the zinc plant was added to make the Zn - Co ratio 12 to 1.

Start with 4.62 liters at 94 gr Zn/L and 7.9 gr Co/L.

Stoichiometrically 1 gr Zn requires 1.62 gr Na_2CO_3.
1 gr Co " 1.80 gr Na_2CO_3.

4.62 x 94 x 1.62 = 704 gr Na_2CO_3 to Zn.
4.62 x7.9 x 1.80 + 66 gr Na_2CO_3 to Co.
770 Total to solution.

Add Na_2CO_3 as solution - 350 gr/L.

To determine when enough Na_2CO_3 has been added, the solution will be tested on phenolphthalein spot paper. A deep red spot shows an excess of reagent.

Time	Temp °C	cc Na_2CO_3	Spot	gr Na_2CO_3	
2:30 P. M.	50		acid		
2:30 to 3:10		2000		700	
3:15			neutral		
3:25 - 3:35		500		175	
3:40			neutral		
3:45 - 3:50		100		105	
3:55			neutral (basic)		Note: This last addition was probably unnecessary as the phenolphthalein was being destroyed by the chlorine in the solution. A filtered sample which had been boiled a minute showed a deep red spot.
4:15 Filtered very well, Dried Calcined at 750°C to a brilliant green.			basic		

No trouble was experienced in making this pigment. Care must be taken to add the Na_2CO_3 slowly in order to avoid getting large curds which hinder agitation. No violent effervescence was observed and the filtration and washing were extremely easy.

Summary

RECOMMENDATIONS

Leaching: It is recommended that the Cobalt Residue be allowed to oxidize in the air before being leached with H_2SO_4. Leach 30 demonstrated the poor extraction which may be expected with fresh material, while No. 30A showed that a serious copper problem would be encountered if the leach residue from fresh material were to be retreated. In connection with copper removal, it is suggested that in plant practice fresh material might be added at the end of a regular leach on thoroughly oxidized residue, in order to precipitate copper. This not only would save zinc dust but might raise the cobalt concentration of the solution. A concentration of between twenty and thirty grams of cobalt per litre is advised, as no trouble is had in precipitating this with hypo and the higher the cobalt concentration the less percentage loss in the purification residue. To obtain the desired concentration the leach could be started with old residue and finished with more recent material of higher cobalt content.

There should be a lead-lined tank equipped with sturdy agitating mechanism as the leach pulp is heavy and requires thorough agitation. Steam coils are desirable to keep the leach warm during the filtration period. During the leaching process considerable heat is generated when the residue is dissolved - enough so that the leach would keep itself sufficiently warm to obtain good extraction. Mulling in a ball mill is desirable but not essential. All leaches on this campaign were run by adding the dry feed, after it was dry ground to pass 10 mesh. The stuff is very soluble and does not require grinding - merely a reasonable separation of one large particle from the other.

Purification: The purification should be run on the warm filtered leach solutions, in a lead lined tank equipped with an agitator and steam coils. Calcine should be used as the basic reagent. This calcine should be thoroughly emulsified before adding to the purification, either in water or in solution. To accomplish this a stout barrel equipped with a portable motorized propeller could be set on top of the tank. If the calcine is not added as an emulsion but as a dry powder, it agglomerates into hard balls upon hitting the solution and is mostly wasted. Potassium permanganate should be used as the oxidizer, and then only enough for iron. The best technique is to add all the calcine and $KMnO_4$ together, adding a little less $KMnO_4$ than is theoretically necessary for iron requirements.

Sponging: This should be done on the filtered purified solution before the addition of hypochlorite so that the resulting sponge will be chlorine free. The solution should be adjusted to a good acid spot and the calculated amount of zinc dust added.

Precipitation of Cobalt: The manufacture of sodium hypochlorite must be carried on in rubber-lined steel or wood tanks. A lead-lined tank on a steel tank will not stand the action of the solution. Chlorine producers recommend steel tanks because of their superior heat dissipating qualities. During the reaction between chlorine and caustic much heat is generated and it is desirable to have cooling coils in the tank thru which cold water can be passed. The rubber lining of the tank and the protective coating on the coils could be a relatively inexpensive commercial coating supplied by specialists in that line - something that could be applied on the job. The tank need not have an air-tight cover - merely a lid to keep whatever chlorine escapes confined to the tank. Not much chlorine is set free if the dry gas is bubbled thru a fairly cool solution of caustic. To introduce the chlorine into the caustic a hard rubber tube, plugged at one end, and drilled with small holes will make an excellent dispersing nozzle. The chlorine may be measured by weighing the cylinders before and after being discharged. The solution may be checked by assaying its oxidizing power (chlorine content) either by the ferrous ammonium sulphate method or the sodium arsenite method. No stirring is necessary as there is an abundance of caustic present to catch the chlorine. A concentration of 240 gr caustic per litre is acceptable. The sodium hypochlorite solution should be admitted very slowly into the purified solutions thru a dispersing tube similar to the one used for the chlorine gas. The precipitation can be conducted in a lead-lined tank equipped with steam coils as the concentration of hypo is so small that there is no danger of destroying the lead. The process should be done in the cold (25-35°C) at the start and enough hypo added, on the caustic basis, to completely precipitate all the cobalt. If any additional hypo is necessary it should be added in 5% excess additions until the cobalt is 0.5 gr/L or lower. On a plant scale it is estimated that 10% to 15% excess will be sufficient. At the time of the last addition, steam should be turned on and the solution heated to 60-65°C. This is not absolutely necessary but heat seems to bring down a little cobalt which persists in remaining in cold solution. However, if steam is too expensive this last operation can be omitted and a longer period of agitation substituted. Good filtration will result either way.

Manufacture of Rinmann's Green: The cobalt and zinc ratio should be adjusted and a solution of sodium carbonate added slowly until precipitation is complete. A lead-lined tank may be used and no particular technique is necessary to obtain an excellent filtration. The calcination furnace will not be discussed here.

Equipment.

The equipment installed in this plant and ready for use with this retreatment scheme is that which is used for cadmium production. It would be necessary to suspend cadmium operations and store the cadmium feed while cobalt oxide production was going on, but this would not be particularly objectionable as the cadmium plant has a capacity far in excess of the feed furnished it by normal zinc operation so that, on a yearly basis, cadmium production could be maintained.

For getting the dry cobalt residue into the plant there are suitable conveyor belts and the necessary storage bins. Following the bins is a ball mill which can be used, if desired, for mulling the feed with wash water stored from filter press operations. A launder runs directly from the discharge of the ball mill to the leach tank. The leach tank is lead lined 15'- 0" in diameter and 11'- 0" deep equiped with a sturdy agitating mechanism consisting of a horizontal cross-beam above the solution, with vertical arms extending down into the solution. The agitator is lead covered and revolves 10 times per minute. The motor driveing the line shaft is a 25 hp. For discharging the tank and forcing the solution through the Shriver press a Coeur d'Alene Hardware centrifugal pump having a 3" inlet and 2" discharge, and making 1800 rpm, is used. Pump is furnished with a 15 hp motor. The Shriver press is an ordinary industrial type filter press, a description of which may be found in any good work on metallurgical machinery. This one, constructed entirely of acid resisting copper-base alloy, has 41 frames and 42 plates each having an effective filtering area of 9 sq.ft. (3' x 3') and capable of withstanding a maximum filtration pressure of 100 lbs. sq.in. The companion tank to the leach tank is the same size, is lead lined and has a similar discharge pump and motor. However the agitating mechanism consists of a long vertical shaft with a horizontal arm suspended eight inches from the bottom of the tank. The shaft and arm are made of steel, lead sheathed, and driven from the same line shaft which drives the leach agitator. It makes 17 rpm. The cadmium spongeing tank is 14'- 0" in diameter and 9'- 0" deep, lead lined. It is equiped with a wooden paddle-type agitator with its own 5 hp motor, revolving 7 times per minute. The discharge pump and motor are the same as for the leach tank. There are two storage tanks of 15'- 0" diameter and 11'- 0" depth which could be used for storing either pregnant or barren solution. There are two additional tanks of 11'-6" diameter and 11'-0"depth which could be used for commercial sulphuric acid (for the leach) and/or wash water from the press. All tanks are lead lined and hold in excess of 20 volume tons. The plant is fitted with a system of valves and pipes so that solution from any tank can be pumped to any other tank in the plant.

Proposed routine for daily operations.

The following routine and time schedule can be used as a basis for plant operation. A 20 volume ton leach would have to be run each 48 hour period in order to utilize 5 tons of feed per 24 hours.

Operation	Time
Leach, adjust specific gravity, remove copper.	10 hrs, 7am to 5 pm
Filter leach solution, wash cake, drop cake, reset press, (will have to be done twice for each leach)	6 hrs, 5pm to 11pm
Purify for Fe and Al	6 hrs, 11pm to 5am
Filter purification, wash cake, drop cake, reset press, (only once for each purification but allow ample time for possible slow filtration)	6 hrs, 5am to 11am
Sponge for cadmium.	3 hrs, 11am to 2pm
Filter sponge, wash. (one press)	3 hrs, 2pm to 5pm
Precipitate cobalt hydroxide	10 hrs, 5pm to 3am
Filter cobalt (One press)	4 hrs, 3am to 7am

The above schedule is for over-all time and is ample for all washing and cleaning operations. Of course it is understood that as soon as one tank is empty another operation is again started. For example when the leach tank is discharged, more acid is drawn and another leach is put in progress while other plant operations are carried on. The same is true of the manufacture of the sodium hypochlorite; a batch for precipitation should be started about the time the leach is one-half finished. This allows plenty of time for the chlorine to bubble through the solution slowly thereby dissipating the heat of formation and minimizing chlorine losses.

COMPILED DATA FOR ESTIMATING COSTS

Batch No. 1

gr acid/gr feed	cc Soln/gr Feed	gr calcine/Liter
504/1040 = 0.484	2200/1040 = 2.12	
498/1040 = 0.479	2010/1040 = 1.94	
705/1450 = 0.486	2700/1450 = 1.87	
708/1450 = 0.488	2800/1450 = 1.93	75/1 = 75
1485/3150 = 0.472	6200/3150 = 1.97	
846/1720 = 0.492	3200/1720 = 1.86	50/1 = 50
2079/4300 = 0.483	7600/4300 = 1.77	
550/1140 = 0.483	2060/1140 = 1.81	
1860/3700 = 0.502	7000/3700 = 1.90	600/7 = 86

Batch No. 2

700/1620 = 0.432	2900/1620 = 1.79	
714/1640 = 0.435	3000/1640 = 1.83	240/3 = 80
714/1580 = 0.451	3000/1580 = 1.90	
2088/4650 = 0.449	8900/4650 = 1.92	180/2 = 90

Batch No. 3

2800/9900 = 0.283	15330/9900 = 1.56	30/1.5=20
1068/3600 = 0.292	6650/3600 = 1.84	133/6.1=22

Batch No. 4

2760/8852 = 0.312	17700/8852 = 1.99	284/12.9=22

COST ESTIMATION - Page 1

	Reasonable Assumptions		Figures Used for Safety Factors
1)	That 1 gram of feed will consume slightly less than 0.5 gr acid.	1)	1 gr of feed will consume 0.5 gr acid.
2)	Sulphuric acid will cost $23-$26 per ton.	2)	Acid will cost $30.00 per ton.
3)	That 1 gram of feed will produce slightly less than 2 cc of leach solution.	3)	1 gram of feed will produce 2 cc of leach solution.
4)	That grams of calcine per liter for purification will not exceed 90, calcine will cost $35.00 per ton.	4)	100 gr calcine per liter will be necessary for purification. Calcine will cost $40.00 per ton.
5)	That $KMnO_4$ requirements will not be over 3 gr/L. (This is equivalent to 3.1 gr Fe/L).	5)	$KMnO_4$ requirements will be 4 gr/L.
6)	That $KMnO_4$ will cost 20¢/lb.	6)	$KMnO_4$ will cost 25¢/lb.
7)	That Chlorine will cost 11¢/lb.	7)	Cl_2 will cost 11¢/lb.
8)	That Caustic will cost 4.72¢/lb.	8)	NaOH will cost 5¢/lb.
9)	That a 15% excess of hypo will be ample to precipitate the cobalt.	9)	A 20% excess of hypo will be added.
10)	That the feed will average, if mixed, approximately 5% Co.	10)	Feed for this illustration at 3.5% Co.
11)	That a leach extraction of 95% of the cobalt can be made.	11)	A leach extraction of 90% of the cobalt.
12)	That at most, 1% to 3% of the available cobalt will be held in the purification residue.	12)	5% of the available cobalt will be held in the Purification residue.
13)	That 1% of available cobalt will be held in the Cd. sponge.	13)	2% of available cobalt will be held in the Cd. sponge.

Reasonable Assumptions		Figures Used for Safety Factors
That no more than 20 gr of Zn dust per liter will be required to precipitate both the copper and cadmium from solution.	14)	25 gr Zn dust per liter is necessary. Zn dust at 6¢.
That solution can be cleaned to 0.5 gr Co or under.	15)	Solution will be taken to 0.5 gr Co/L.
That in plant practice 35% excess chlorine in the hypochlorite will suffice to give a good product.	16)	A 40% excess chlorine solutiom will be used.
An over-all recovery of 85% of the Cobalt can be consistently made.	17)	Over-all recovery of 80% of the cobalt.
That the final product can be sold from $1.10 per lb. to $1.55 per lb. of contained Co.	18)	Cobalt sold at $1.00 per lb.
That 5 to 10 tons of Cobalt residue (feed) could be put thru process per day.	19)	5 tons feed per day worked.

A few words of explanation concerning the "reasonable assump-
ns" should be given at this time. The metallurgical relationships
e, naturally, taken from the data of the investigation. The cost of
lorine and caustic are the quotations of a Tacoma electrochemical
mpany for material laid down in Kellogg, (freight included), in less
an carload lots. There is a substantial saving in freight if car-
ad lots are ordered. The cost of $KMnO_4$, calcine, zinc dust and
id are taken from past experience.

The final cobalt product stands an excellent chance of being
ld for more than $1.00 per lb. of contained cobalt. The lowest direct
fer made by consumers of cobalt oxide was $1.10 per lb. of cobalt and
highest offer made was $0.75 per lb. of 48% Co material. This
ter figure represents a quotation of $1.56 per lb. of cobalt. Another
er was from $1.25 to $1.50 per lb. of contained cobalt depending on
impurities. Every consumer contacted wanted all the material that
ld be supplied, some as much as 100,000 lbs. per year.

COST CALCULATION

Cobalt Balance

	Lbs. Co.	
ton of Cobalt Residue @ 3.5% Co	70.00	
0% remaining in leach residue		7.00
alt extracted by leach (90%)	63.00	
% of available cobalt in Purification Residue		3.15
alt in 2 Vol. Tons of Purified Solution	59.85	
% of available Cobalt in Cadmium Sponge		1.20
alt in 2 Vol. Tons - Solution to Precipitate	58.65	
o left in 2.65 vol.tons of barren Sol'n at 1#/V.T.		2.65
recovered in final product (an over-all recovery of 80%)	56.00	

Reagent Cost

	Unit Cost	Total Cost
ton of feed (Co Res.) consumed 1000 lb. acid	$30.00 ton	$15.00
ton feed produced 2 vol. tons - sol'n requiring:		
200 lbs. Calcine/V.T.	.02 lb.	8.00
8 lbs. $KMnO_4$/V.T.	.25 lb.	4.00
50 lbs. Zinc Dust/V.T.	.06 lb.	6.00
ton feed yields 58.65 lbs. Co to be precipitated by sodium hypochlorite at,	23.275¢/Lb.Co.	13.70

Figured as follows:

Lbs. chlorine-theoretical for 1 lb. Co	0.6013 lbs.
40% excess for $Zn(OH)_2$ retardation	0.2445 "
	0.8458 "
20% excess of total for inefficiency	0.1692 "
Total chlorine per lb. Co	1.0150 x 11¢=11.165¢
Lbs. caustic-theoretical for 1 lb. Co	2.036 lbs.
20% excess of theoretical for inefficiency	0.407 "
Total NaOH per lb Co	2.443 x 5¢ = 12.210¢

Total cost of hypo per lb. of Co=11.165¢+12.210¢=23.375¢

al cost of reagents per ton of feed, thru plant - - - - - - ---	$46.70
venue from cobalt sold at $1 per lb. - - - - - - - - - - - - - - -	56.00
rgin per ton of feed, to apply on labor,power,maintenance, etc.-	-$ 9.30

Cost calculation using 5.0% Cobalt in Feed

	lbs Co	
One ton of Co residue @ 5.0% Co	100	
10% remaining in leachbresidue		10
Cobalt extracted by leach (90%)	90	
5% of available cobalt in Purification Res.		4.5
Cobalt in 2 vol.tons of Purified Soln.	85.5	
2% of available cobalt in Cadmium sponge		1.71
Cobalt in 2 vol.tons solution to Precipitate	83.79	
Cobalt left in 2.52 vol tons Barren at 1.5 #/vt		3.79
Cobalt recovered in final product	80.00	

Reagent cost	Unit cost	Total cost
One ton of feed consumes 1000 lb acid	$30.00 ton	$15.00
One ton feed produces 2 vol tons sol'n requiring; 200 lbs calcine/vt	.02 lb	8.00
8 lbs KMNO$_4$ /vt	.25 lb	4.00
50 lbs Zinc dust/vt	.06 lb	6.00
One ton feed yields 83.79 lbs of cobalt to be precipitated by sodium hypochlorite at 23.375 cents per lb of cobalt		19.50
Total cost of reagents per ton of feed thru plant		$52.50
Revenue from cobalt sold at $1 per lb.		$80.00
Margin per ton of feed, to apply on plant charges		$27.50

SUMMARY

There has been developed ahydrometallurgical procedure for the retreatment of cobalt residue in order to recover the cobalt cadmium and zinc therefrom. This procedure is entirely practical and with very little additional equipment could be put into effect using the machinery and equipment already installedat this plant.

The economic success of the plan, if the entire cost is to be borne by the cobalt, depends upon keeping the grade of feed reasonably high (5% Co) and getting at least $1 per lb. for the cobalt. Neither of these should be hard to do.

The first cost sheet was inserted to show the very minimum of Co in the feed that could be successfully worked. The $9.30 per ton of feed would barely pay labor and power. The second cost sheet shows more nearly the return which could be expected by practical operations. A margin of $27.50 per ton of feed, on a 5 ton per day basis, allows ample for labor, power, taxes, depreciation, etc., and for an attractive profit. In all fairness it should be pointed out that as the cobalt in the feed is raised, and the extraction improved, the hypochlorite cost also goes up. The 23.375¢ per lb. of cobalt is inescapable. Also, no charge is made for the feed to the plant, the cost of this item having been charged, previously, to zinc production. This cost omission is balanced by the fact that the cadmium and zinc content of the cobalt residue is recovered without charge.