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# THE EXTRACTION OF COBALT, NICKEL, COPPER AND SILVER FROM ORE AND SPEISS FROM DELORO SMELTING AND REFINING CO. LTD., ONT.

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by

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MINERAL DRESSING AND PROCESS METALLURGY DIVISION

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Mines Branch Investigation Report IR 58-188

THE EXTRACTION OF COBALT, NICKEL, COPPER AND  
SILVER FROM ORE AND SPEISS FROM DELORO SMELTING  
AND REFINING CO. LTD., ONTARIO

by

G. Thomas<sup>\*</sup> and T. R. Ingraham<sup>AA</sup>

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SUMMARY OF RESULTS

Samples of roasted Deloro speiss and ore, containing 18-22% Co, 4-7% Ni, 3-4% Cu and 150-850 oz Ag/ton, were leached with sulphuric acid in a stainless steel autoclave and in a glass pachuca. Extractions of cobalt, nickel, and copper in excess of 95%, were obtained by single stage leaching under vigorous reaction conditions in an autoclave, or by cyclic leaching under milder conditions in either an autoclave or in a pachuca. The extraction of silver was very irregular and varied from over 96% to less than 1%. The identity of the silver compounds in the residues was not established, but it was shown that the silver compounds could be extracted with cyanide.

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## INTRODUCTION

### Shipments and Instructions

Mr. C. R. Whittemore, chief metallurgist at the Deloro Smelting and Refining Co. Ltd., requested in a letter dated September 19, 1955, that leaching tests be done on their roasted speiss and ore for the extraction of cobalt, nickel, copper, and silver. Various samples for testing were submitted by the Company from 1955 to 1957. During this period, details of the experimental procedures and results were either sent to Mr. Whittemore, or discussed with him during his frequent visits to the Mines Branch. To decrease the amount of test work required to determine the optimum leaching conditions for speiss and ore, the preliminary experiments were statistically designed by Mr. R. C. Shnay of the Mines Branch Ferrous Section, on the basis of information supplied to him.

### Chemical Analyses of Samples

The chemical analyses of the various samples of roasted ore and speiss are given in Table 1. Speiss B and later speiss C, were received when the supply of speiss A had become depleted. Speiss D was a special low-chloride sample.

TABLE 1  
Chemical Analyses of Ore and Speiss

Sample	Ag (oz/ton)	Co (%)	Ni (%)	Cu (%)	Fe (%)	Pb (%)	As (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	S (%)	Cl (%)
Ore	146	18.3	4.5	2.9	12.3		12.7	16.2	13.4	0.2	
Speiss A	669	18.6	4.6		28.1						
Speiss B	684	19.4	5.4	3.9	27.6						
Speiss C	861	18.6	7.3	3.6	21.8	2.5	11.3				tr.
Speiss D	472	22.4	6.8	3.2	22.1	0.7					0.008

#### DETAILS OF INVESTIGATION

##### Leaching Procedure

The pressure leaching tests were done in a four litre stainless steel autoclave equipped with a mechanical stirrer. The sample of speiss or ore was heated, together with sulphuric acid and water, to temperatures of 100 to 200°C, under oxygen pressures of up to 160 psig, for periods of up to 430 min. The resultant slurry was centrifuged, and the solid residue was repulped and washed several times with a 1% H<sub>2</sub>SO<sub>4</sub> solution. The washed solid residue, and the combined leach and wash liquors, were analyzed chemically for various constituents.

In certain experiments, the leaching was done in an electrically heated glass pachuca which was fitted with a sintered glass disc in its conical base. Oxygen was passed through the disc

to agitate, and to oxidize the slurry of speiss and acid. Loss of moisture during the leaching was prevented by a condenser at the top of the pachuca.

#### Preliminary Autoclave Leaching Tests (Speiss A)

In accordance with the request from Deloro, 235 g samples of speiss or ore were heated in an autoclave with 275 g 95%  $H_2SO_4$  and 845 g  $H_2O$ . The chemical analyses for the preliminary tests were done at Deloro. The results of these fractional replicate tests on the ore and speiss A are given in Table 2. The leaching efficiency, as given in Table 2, was calculated from the amount of each ion found in the leach liquor, in relation to the combined amount found in the leach liquor and the leach residue.

TABLE 2

#### Preliminary Leaching Tests on Ore and Speiss A

Test	Sample	Reaction Conditions			% Extraction				Metallurgical Balance			
		Temp (°C)	O <sub>2</sub> (psig)	Time (min)	Ag	Co	Ni	Fe	Ag	Co	Ni	Fe
1	Ore	102	120	120	73	87	93	53	96	104	95	98
2	"	102	160	60	71	86	90	47	98	106	93	98
3	"	121	120	60	68	86	92	41	95	104	98	101
4	"	121	160	120	66	86	91	21	97	104	92	96
5	Speiss A	102	120	120	93	41	62	12	96	89	133	103
6	"	102	160	60	92	42	56	9	96	95	119	103
7	"	121	120	60	94	43	55	12	96	93	128	102
8	"	121	160	120	95	49	64	17	97	93	120	102

The leaching conditions for tests 1 to 4 with ore, were duplicates of those for tests 5 to 8 with speiss A. Table 2 shows that cobalt, nickel and iron were extracted more readily from the ore than from the speiss. On the other hand, the silver was extracted more readily from the speiss than from the ore.

The data from the leaching of the speiss indicated that the effects of the reaction variables on extraction, were different for silver than for the other metals. A mathematical analysis of the data by Mr. Shnay suggested that an approach to maximum silver extraction, together with an improvement in the extraction of the other metals, might be obtained by using the reaction conditions as shown in test 9 Table 3. While awaiting the chemical analysis, and the mathematical analysis of the data from this test, the effects of higher temperatures (up to 200°C) were investigated. The chemical analyses for these and all subsequent tests were done by the Analytical Chemistry Section of the Mines Branch.

TABLE 3

Additional Leaching Tests on Speiss A

Test	Reaction Conditions			% Extraction				
	Temp (°C)	O <sub>2</sub> (psig)	Time (min)	Ag	Co	Ni	Cu	Fe
9	163	140	160	90	75	84	88	38
10	175	120	140	90	79	86	89	40
11	200	120	140	7	90	92	93	31
12	200 <sup>A</sup>	120	140	1	84	89	90	32

<sup>A</sup> Temp at 200°C for 140 min and then at 120°C for 30 min.

Table 3 shows that the experimental conditions chosen for test 9 were suitable for obtaining high extractions of all the valuable metals from speiss A. These extractions were, in general, much higher than those obtained in the initial tests of Table 2. By increasing the reaction temperature from 163°C to 175°C, as shown in tests 9 and 10, a slight increase in the extraction of the metals was obtained. A further increase in the extraction of the cobalt, nickel and copper was obtained when the reaction temperature was increased to 200°C as shown in test 11. However, at 200°C the silver extraction was only 7%.

Certain salts with retroflex solubility characteristics, are relatively insoluble at high temperatures but are very soluble at low temperatures. To determine if this behaviour of low solubility at high temperature were responsible for the small extraction of silver in test 11, the test was repeated (test 12) using an initial leaching temperature of 200°C and a final leaching temperature of 120°C. The extraction of silver in this run, as shown in Table 3, was only 1%, thus showing that retroflex solubility was not the explanation for the poor silver extraction.

The decrease in silver extraction, from 90% to 1%, does not appear to be related to the solubility of silver sulphate in acid solutions. For the tests listed in Table 3, 1 litre of 3 M  $H_2SO_4$  was used to treat the 235 g speiss. The speiss contained 5.4 g silver which, on complete sulphation, would form 7.8 g silver sulphate.



After the leaching stage of the tests, the leach residues were centrifuged and repulped several times with 1%  $H_2SO_4$ . The solubility of silver sulphate (A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Van Nostrand, New York, 1940) in 3 M and 0.005 M  $H_2SO_4$  is reported to be 9.7 g/l and 8.1 g/l respectively. According to this, the silver sulphate from the speiss should be completely soluble in the leach solutions. It therefore seems unlikely that low silver extractions, e.g., 1%, were due to an insufficiency of liquor to dissolve silver sulphate.

#### Leaching of Ore and Speiss B

After the supply of speiss A was depleted, test work was done on speiss B. A comparison of test 13, Table 4 with test 9, Table 3, shows that the response of speiss B to leaching was similar to that of speiss A.

Grinding of the speiss had little effect on the leaching process. For example, when speiss B, 10% + 100 mesh and 49% - 325 mesh, was ground to 99% - 325 mesh as in test 14, no appreciable change in metal ion extraction was obtained. Similarly, no significant increase in metal ion extraction was obtained (test 15) when additional acid was used.

TABLE 4

Leaching of Speiss B(235 g speiss, 845 g H<sub>2</sub>O, 163°C, 140 psig O<sub>2</sub>, 160 min)

Test	Reaction Conditions		% Extraction				
	Grind (% - 325 mesh)	H <sub>2</sub> SO <sub>4</sub> (g)	Ag	Co	Ni	Cu	Fe
13	49	275	84	81	89	88	33
14	99	275	85	81	89	87	32
15	99	325	89	80	89	88	38

A series of experiments was done with ore and speiss B, to determine the effect of acid concentration on the leaching process. For these experiments, the amount of acid was kept constant but the amount of water was decreased. Sufficient water was used in each test to prevent the slurry from caking. The experimental leaching conditions were similar to those previously found to be reasonably satisfactory. The results of these tests are given in Table 5.

TABLE 5

Leaching of Ore and Speiss B(470 g ore or speiss, 550 g H<sub>2</sub>SO<sub>4</sub>, 140 psig O<sub>2</sub>, 160°C, 160 min)

Test	Sample	H <sub>2</sub> O (g)	H <sub>2</sub> SO <sub>4</sub> (mole/l)	% Extraction				
				Ag	Co	Ni	Cu	Fe
16	Ore	700	5.7	72	99	99	93	78
17	"	600	6.2	74	99	99	99	90
18	Speiss B	800	5.1	96	83	91	89	65
19	"	700	5.7	20	87	92	86	63
20	"	600	6.2	26	99	96	99	85

Table 5 shows that by leaching the ore under pressure with the 6.2 molar sulphuric acid solutions, 99% of the cobalt, nickel, and copper was dissolved. The extraction of silver from the ore, as in previous tests, was slightly below 75%.

Over 96% of the cobalt, nickel and copper was leached from speiss B by the use of 6.2 molar sulphuric acid. For silver, seemingly erratic extractions were obtained when speiss B was leached with the sulphuric acid solutions. In test 18, a silver extraction of 96% was obtained with the 5.1 molar acid. When more concentrated acid was used, tests 19 and 20, there was an increase in the dissolution of cobalt, nickel and copper, but the silver extraction was decreased to about 20%.

#### Leaching of Speiss C and Speiss D

Speisses C and D were leached under various experimental conditions. Initially, the reaction conditions and the proportions of the various reagents were the same as those used in test 20 with speiss B. In these experiments, tests 21 and 22 in Table 6, extractions in excess of 95% were obtained from speisses C and D for all the metals except silver.

Several experiments were done with speiss D, using more rigorous reaction conditions. In these experiments, the conditions were: a reaction temperature of 200 °C, test 23; a more concentrated acid solution, test 24; a reaction period of 430 min, test 25; a large excess of acid, test 26. In general, these stringent

reaction conditions increased the extractions of cobalt, nickel and copper slightly, and extractions of up to 99% were obtained. The extraction of silver was somewhat erratic; the maximum silver extraction was 84%.

TABLE 6  
Leaching of Speiss C and Speiss D  
(600 g speiss, 140 psig O<sub>2</sub>)

Test	Sample	Time (min)	Temp (°C)	H <sub>2</sub> SO <sub>4</sub> (g)	H <sub>2</sub> O (g)	% Extraction			
						Ag	Co	Ni	Cu
21	Speiss C	160	160	700	750	89	96	97	95
22	Speiss D	160	160	700	750	64	95	95	96
23	"	160	200	700	750	65	96	96	97
24	"	160	160	700	550	24	96	95	98
25	"	430	160	700	750	29	97	95	98
26	"	160	160	1150	1250	84	97	94	99

To improve the extraction of silver, cyclic leaching tests were done with speiss D, using the conditions as given in Table 7. In these tests, the residual solids from each cycle were re-leached, together with a fresh ore charge, in the subsequent cycle. In the cyclic leaching, Table 7, the silver extraction decreased to 3% in the third cycle, for an over-all silver extraction of 41%. However, the extractions of cobalt, nickel and copper were uniformly high at about 95%.

TABLE 7Cyclic Autoclave Leaching of Speiss D(600 g speiss, 700 g H<sub>2</sub>SO<sub>4</sub>, 750 g H<sub>2</sub>O, 140 psig O<sub>2</sub>, 160°C, 430 min)

Test	Cycle	% Extraction			
		Ag	Co	Ni	Cu
27	1	64	95	95	96
28	2	42	97	92	97
29	3	3	96	96	96

Pachuca Leaching Tests

In certain previous leaching tests, the extraction of silver appeared to decrease with increasingly rigorous leaching conditions. Because of this, a number of tests were done with a glass pachuca to provide mild leaching conditions. Furthermore, the possibility existed that the low extractions of silver from the speiss, were due to freshly dissolved silver reacting with the stainless steel autoclave to precipitate metallic silver. This reaction would be prevented by the use of the glass pachuca. In the pachuca leaching tests, the slurry of speiss, water, and acid, was heated to its boiling point of 110 to 120°C, and was agitated by the passage of oxygen through the slurry.

In the first test, the rate of the leaching reaction was studied. Samples of the slurry were removed at intervals and filtered. From the analysis of the filtrate, the percentage extraction of the cobalt and silver was calculated, with the results as shown in Table 8. This table shows clearly that the leaching process was rapid, with about 80% of the reaction occurring within the first half hour.



The extraction was, however, increased by the use of longer leaching periods.

TABLE 8

Rate of Leaching of Speiss in a Pachuca  
(300 g speiss C, 350 g  $H_2SO_4$ , 375 g  $H_2O$ , 110-120°C)

Test	Time (hr)	% Extraction	
		Ag	Co
30	0.5	78	79
"	2	79	86
"	5	84	95

Speiss C was used for two separate pachuca leaching tests of three hours and eight hours duration. The results of these tests, Table 9, show that although the eight hour leaching period, increased the extraction of cobalt, nickel and copper, it decreased the extraction of silver. Since the pachuca was made of glass, the low extraction of silver in test 32 could not be attributed to the precipitation of silver by steel.

TABLE 9

Pachuca Leaching of Speiss C  
(200 g speiss C, 240 g  $H_2SO_4$ , 250 g  $H_2O$ , 110-120°C)

Test	Time (hr)	% Extraction			
		Ag	Co	Ni	Cu
31	3	81	82	82	82
32	8	33	87	88	87

Cyclic Pachuca Leaching Tests

In a series of tests, speiss D was leached with acid for two hours in the pachuca. The leach residue from each cycle was returned, with fresh speiss and acid, to the pachuca. In the fourth cycle the residue only, without fresh speiss, was returned to the pachuca for leaching with fresh acid. The results of these tests are given in Table 10.

TABLE 10

Cyclic Pachuca Leaching of Speiss D

(100 g speiss D, 120 g H<sub>2</sub>SO<sub>4</sub>, 125 ml H<sub>2</sub>O, 120 min, 110-120°C)

Test	Cycle	Residue (g)	% Extraction			
			Ag	Co	Ni	Cu
33	1	32	0.3	80	77	84
34	2	61	0.2	64	68	78
35	3	83	0.2	65	70	81
36	4	39	3.1	69	77	87
			3.6 <sup>A</sup>	95 <sup>A</sup>	97 <sup>A</sup>	99 <sup>A</sup>

<sup>A</sup> Over-all percentage dissolution

The cyclic leaching of speiss D gave very low extractions of silver. However, moderate dissolution of cobalt, nickel and copper were obtained in each cycle. Since the residues were recycled, the over-all extraction for each of these three metals was over 95%.

Acid Consumption for Re-leaching

The cyclic tests showed that when leach residues were re-leached in a pachuca, high over-all extractions of cobalt, nickel and copper were obtained. To determine the amount of acid required for the re-leaching, the following series of tests was done. A 500 g sample of speiss D was leached in the pachuca to provide about 150 g leach residue, from which 30 g samples were re-leached with various amounts of sulphuric acid. Table 11 gives the results of these tests.

TABLE 11

Acid Requirements for the Re-leaching of Residues  
(500 g speiss D or 30 g residue, 120 min, 110-120°C)

Test	Charge			% Extraction			
	Material	H <sub>2</sub> SO <sub>4</sub> (g)	H <sub>2</sub> O (g)	Ag	Co	Ni	Cu
37	Speiss D	585	625	0.4	79	81	90
38	Residue	88	100	8.4 <sub>8.8x</sub>	82 <sub>96x</sub>	75 <sub>95x</sub>	70 <sub>97x</sub>
39	Residue	66	75	1.7 <sub>2.1x</sub>	75 <sub>95x</sub>	69 <sub>94x</sub>	62 <sub>96x</sub>
40	Residue	44	50	1.2 <sub>1.6x</sub>	74 <sub>95x</sub>	64 <sub>93x</sub>	61 <sub>96x</sub>
41	Residue	22	50	0.2 <sub>0.6x</sub>	19 <sub>83x</sub>	21 <sub>85x</sub>	20 <sub>92x</sub>

<sup>x</sup>Over-all percentage extraction

Table 11 shows that 90% of the copper in test 37 was extracted from the speiss, and therefore 10% was left in the residue. On leaching the residue, test 38, 70% of this residual copper was dissolved for an over-all extraction of 97%. The various tests of Table 11 show that when leach residues were re-leached with suitable

amounts of fresh acid, the over-all extractions for cobalt, nickel and copper were about 95%.

The amount of acid used for re-leaching in test 40 was sufficient to give high over-all extractions of cobalt, nickel and copper. The use of additional acid for re-leaching, as in tests 38 and 39, did not appreciably increase the extraction, but with less acid as in test 41, the extraction was decreased considerably. Hence the amount of acid used for test 40 corresponded to maximum extraction, consistent with minimum acid consumption. In test 40, the proportion of acid to solid used in leaching the residue was about the same as that used in test 37, for the initial leaching of the speiss.

#### Silver in the Leach Residues

In the diverse leaching tests, the extraction of silver was found to be extremely variable. A number of tests were done to determine the cause of the erratic silver extractions. Additional experiments were also done to recover the silver from the leach residues. The results of these experiments are given in the following sub-sections.

##### 1. Analysis of Leach Solutions

When Deloro speiss was leached with sulphuric acid, the leach solutions were found to contain various ions in both their higher and lower oxidation states. There was therefore, the possibility that the silver, after its initial dissolution was reduced, and precipitated in its metallic form. The chemical analysis of

various leach liquors, prior to their dilution by the washing of the residues, is given in Table 12.

TABLE 12

Chemical Analysis of Leach Liquors

Test	Reaction vessel	Chemical Analysis, (g/l)					Ag Extraction (%)
		Fe <sup>+++</sup>	Fe <sup>++</sup>	As <sup>+++++</sup>	As <sup>+++</sup>	Ag <sup>+</sup>	
15	Autoclave	23	0.4	9	0.5	4.6	89
19	"	77	0.7	48	0.1	2.1	20
31	Pachuca	86		43	2.5	12.8	81
32	"	91		50	1.2	5.9	33

In the two autoclave leaching tests, 15 and 19, the greater silver extraction occurred in the liquor which had the greater  $As^{+++}/As^{+++++}$  and the greater  $Fe^{++}/Fe^{+++}$  ratios. Similarly, in the pachuca leaching tests 31 and 32, the greater extraction of silver was in the liquor having the greater  $As^{+++}/As^{+++++}$  ratio. These data do not support the assumption that low silver extractions might be due to the reducing conditions in the leach liquors.

Arsenic was present in leach liquors in rather large amounts as shown in Table 12. Because of this, the precipitation of insoluble silver arsenate was considered as a possible cause of low silver extractions. To determine if this were the cause, a sample of filtered leach liquor, which contained 3 g  $Ag^{+}/l$  and 25 g  $As^{+++++}/l$ , was heated to 200°C in an attempt to precipitate silver arsenate. By filtration, a small amount of a solid residue was recovered. An



X-ray diffraction pattern indicated the residue to be scorodite,  $\text{Fe}_2\text{O}_3 \cdot \text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . A semi-quantitative spectrographic analysis showed the residue to contain approximately 10% Fe, 10% As, and only 0.3% Ag. Although the arsenic in the liquor caused the precipitation of some iron, the amount of silver in the precipitate was almost negligible.

## 2. X-ray Diffraction Patterns of Residues

Since the extraction of silver from Deloro speiss was frequently low, the leach residues often had a high percentage of silver. It seemed likely that if the silver compounds in the residues could be identified, improvements in the leaching procedure could be devised. Consequently, several leach residues were submitted for analysis by X-ray diffraction, with the results as shown in Table 13.

TABLE 13

### X-ray Diffraction Analysis of Leach Residues

Test Residues	Leach Sample	Components of Residues			
		Major	Minor	Trace	Ag(%)
32	Speiss C	$\text{PbSO}_4, \text{Fe}_3\text{O}_4, \text{AgCl}$			9
30	" C	$\text{PbSO}_4$	$\text{Fe}_3\text{O}_4, \text{AgCl}$		3
24	" D	$\text{Fe}_3\text{O}_4$	$\text{PbSO}_4$	$\text{SiO}_2$	10
24-2	" D	$\text{PbSO}_4$	$\text{SiO}_2$		18

Silver chloride was identified in certain residues obtained by leaching speiss C. The presence of insoluble silver chloride in the residue was probably due to the contamination of the speiss during its treatment at Deloro, where sodium hypochlorite is used as an oxidizing agent.

Speiss D was free of hypochlorite contamination, and contained only 0.008% chlorine, or sufficient to combine with less than 2% of the silver in the speiss. On leaching speiss D, test 24, a residue was obtained which contained 10% silver, or 76% of the silver from the speiss. The main silver compound in the residue was, therefore, not silver chloride. When this residue was re-leached, test 24-2, a considerable amount of iron was dissolved, and the final residue contained 18% silver. Unfortunately, in neither of these residues was silver in any form definitely identified by X-ray analysis. This lack of identification, despite the high silver content, is attributed to the silver being present in an amorphous, non-crystalline condition.

### 3. Distillation of Components of Residue

An attempt was made to change the amorphous silver compounds into crystalline silver compounds, by heat treatment of a leach residue. A sample of residue obtained by leaching speiss D, in test 29-2, was placed in a horizontal silica tube, which was closed at one end. The tube was placed in a split oven, which was gradually heated to 1000°C in 100° intervals. The silica tube, with its open

end projecting from the oven and acting as an air-cooled condenser, was removed stagewise during the heating period. By this treatment, various volatile components were removed, and deposited in bands along the cool end of the silica tube. The x-ray diffraction analyses of the various deposits showed the volatile components to be S,  $As_2O_3$ , PbS, and Pb. Although the leach residue contained 11% silver, no silver compound, or metallic silver, was identified in the volatile fractions or in the oven residue.

#### 4. Re-leaching of Residues

To improve the extraction of silver, certain leach residues from previous tests were re-leached with fresh sulphuric acid in a pachuca, with results as given in Table 14. For ease of comparison, the silver extractions obtained in the previous tests are also included in this table. The test numbers denote the previous tests which provided the leach residues for the re-leaching tests.

TABLE 14

Re-leaching of Leach Residues

(Solid:liquid ratios as in test 29, 120 min, 110-120 °C)

Test	% Ag Extraction		
	Previous	Present	Over-all
31-2	81	88	97
23-2	65	83	94
25-2	29	40	57
24-2	24	7	29
29-2	3	18	20

Previous tests have shown that by the re-leaching of residues, high over-all extractions of cobalt, nickel and copper were generally obtained. In certain instances, e.g. Table 14 tests 31-2 and 23-2, high over-all extractions of about 95% were also obtained for the silver. The limited tests of Table 14 indicate that residues from tests in which moderate dissolution of silver occurred, can be re-leached to give high over-all extraction of the silver. When low extractions of silver were obtained in the initial leaching tests, the re-leaching of residues from these tests gave poor over-all extractions of silver.

#### 5. Cyanidation of a Residue

In a previous experiment, test 29-2, a leach residue was re-leached with sulphuric acid. Due to the low silver extraction, the sulphuric acid re-leach residue contained 11% silver. Tests were done to dissolve the silver in this residue by cyanidation. Samples of the residue were agitated in open flasks for 60 hr at room temperature, using dilute lime solutions containing various amounts of sodium cyanide. In one test, the cyanide was replaced by sodium thiosulphate, and in another test, a de-aerated solution in a stoppered flask was used. The results of these tests are given in Table 15.

TABLE 15

Cyanidation of a Leach Residue(1 g residue of test 29-2, 0.1 g CaO, 100 g H<sub>2</sub>O, 60 hr, 25°C)

NaCN (g)	0.10	0.15	0.25	1.0	0.25 <sup>A</sup>	1.0 <sup>AA</sup>
Ag dissolved (%)	56	90	91	93	89	0.4

A De-aerated solution.

AA 1.0 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O instead of NaCN

The sulphuric acid leach residue contained 11% Ag, or over 3000 oz Ag/ton. Table 15 shows that 90% of the silver was dissolved from 1 g leach residue, which contained 0.11 g Ag, by the use of 0.15 g NaCN. Very little improvement in the extraction was obtained by additional cyanide. Although not investigated, it might be possible to re-leach with fresh cyanide, to obtain an improved over-all extraction of silver.

Sodium thiosulphate, or "hypo", is a solvent for many silver salts. However, as shown by Table 15, the thiosulphate was decidedly inferior to cyanide in treating the Deloro residue. Table 15 shows that the silver in the residue was dissolved by a de-aerated cyanide solution. Since oxygen was not required for the dissolution, the silver in the residue was probably present in the oxidized state as a silver salt and not in the metallic state. Although the identity of the silver salt has not been established, the salt has been shown to be readily soluble in dilute cyanide solutions.



## CONCLUSIONS

Samples of roasted Deloro speiss and ore, containing 18-22% Co, 4-7% Ni, 3-4% Cu and 150-850 oz Ag/ton, were leached with sulphuric acid in a stainless steel autoclave and in a glass pachuca, for the extraction of valuable metals. From a mathematical analysis of a few fractional replicate tests, an attempt was made to establish the most suitable experimental leaching conditions. However, the statistical method was not fully investigated, due to difficulties encountered with the erratic experimental recovery of the silver. The metal extractions were, in general, similar for each of the speisses, and were somewhat lower from the speiss than from the ore.

Fine grinding, and excess amounts of acid had only a slight effect on metal extraction from Deloro speiss, but an improved metal recovery was obtained by increasing the acid concentration. It was found that when speiss was pressure leached in an autoclave for 160 min at 160°C under 140 psig oxygen pressure, with the weights of speiss:H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O in the ratio of about 1:1.2:1.3, the extraction of cobalt, nickel and copper were 99%, 96% and 99% respectively.

Silver extractions of 96% were obtained in certain experiments, but in other tests, the extraction of silver was less than 1%. It was not found possible to select reaction conditions that would consistently give high extractions of silver. The use of more vigorous leaching conditions, such as increases in reaction

time, temperature, or acid concentration, frequently but not invariably gave lower silver recoveries.

Since the extractions were always incomplete, the leach residues always contained metal values. In a series of cyclic autoclave tests, it was found possible to recycle the residue, for re-leaching in the autoclave with fresh speiss and acid. In these cyclic leaching tests, the extraction of cobalt, nickel and copper was over 95%.

By the leaching of Deloro speiss at about 115°C in an open pachuca, a metal extraction of approximately 75% was obtained. In the cyclic leaching tests, whereby the leach residue was re-leached by sending it back to the pachuca with fresh speiss and acid, the extraction of cobalt, nickel and copper was over 95%. The leaching reaction in the pachuca was found to be rather rapid, with most of the leaching having occurred within one half an hour.

Approximately the same proportion of acid to solid, that was used for the initial leaching of speiss, was found to be adequate for the re-leaching of residues. Hence the acid requirements for the re-leaching of residues, as in a commercial cyclic leaching process, could be readily determined. Although the re-leaching process gave high extractions for cobalt, nickel and copper, the extraction of silver by cyclic leaching in a pachuca, as in an autoclave, was very erratic.

No suitable explanation was obtained for the low recoveries of silver. The formation of silver arsenate at high leaching

temperatures did not seem to be the cause of low silver recoveries since the heating of filtered leach liquors, although causing the precipitation of ferric arsenate, did not precipitate silver arsenate. The very low silver recoveries were not due to an insufficiency of acid, since low silver recoveries were obtained when residues were re-leached with additional fresh sulphuric acid. The low extraction did not appear to be the result of the precipitation of metallic silver, due either to the use of steel equipment, or to the presence of reducing components in the leach liquor. Contrariwise, a silver salt instead of metallic silver was probably present in the leach residue, since the silver could be extracted by cyanidation of the leach residues with de-aerated solutions.

Silver chloride was identified in certain leach residues by means of X-ray diffraction patterns. In these instances, the chloride was probably derived from the sodium hypochlorite used at Deloro. With chloride-free speiss, the identity of the silver compounds in leach residues, containing up to 18% silver, could not be established. The silver compounds in the residues were likely present in a finely-divided amorphous condition. The heating of a leach residue to 1000°C, to produce a crystalline silver residue, or to evaporate and condense a crystalline silver deposit, was unsuccessful.

The silver in leach residues was found to be readily soluble at room temperature in dilute cyanide solutions. The silver extraction by cyanidation was over 90%. Although not investigated,

perhaps re-cyanidation would improve this silver extraction. Smelting of the residues would be another method for the recovery of silver from leach residues.

In summary, it has been found possible to extract up to 99% of the cobalt, nickel and copper, by treating roasted speiss with sulphuric acid under oxygen pressure at elevated temperatures in an autoclave. Instead of a single leaching stage with vigorous leaching conditions to obtain this extraction, a similar recovery can be obtained by a cyclic leaching process with mild leaching conditions, either in an autoclave or in a pachuca. Residues from the sulphuric acid leaching can be treated by cyanidation for the recovery of the silver.

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GT:TRI:CL