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MINES BRANCH INVESTIGATION REPORT IR 65-17

**COPPER AND ZINC CONTENTS OF WASTE
WATERS AND RECEIVING STREAM WATERS
AT BRUNSWICK MINE, NEW BRUNSWICK**

by

J. F. J. THOMAS & W. J. TRAVERSY

MINERAL PROCESSING DIVISION

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COPPER AND ZINC CONTENTS OF WASTE WATERS
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SUMMARY OF RESULTS

Chemical analyses of receiving stream waters at the Brunswick mine show abnormally high zinc contents in the South Little and Little Rivers. This pollutant, as well as decreased pH and mineralization in these rivers, is due to inflow of polluted waters from a source or sources other than the effluent from the mine treatment-ponds.

The precipitate that forms in the treated mine waste water upon acidification is organic matter which was not further identified. No evidence was found that this material significantly interferes with tests for zinc and copper in the waters. A high lead content was found in the treated waste effluent.

Recommendations are made for future investigation of the source of the pollutants in the South Little River and for the monitoring of all waters for lead in addition to zinc and copper.

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INTRODUCTION

For some time the Industrial Waters Section, Mineral Processing Division, Mines Branch, has been monitoring mine waste and receiving stream waters for their copper and zinc content, at several base metal mining operations in New Brunswick. These investigations, carried out at the request of the Department of Fisheries and the New Brunswick Water Authority, are preliminary to research on methods of reducing the pollution of receiving streams by mining operations in Canada.

Except for a few samples collected in 1963, monitoring of receiving streams at the Brunswick Mining and Smelting Co. Ltd's property near Bathurst did not begin until about June 1964, when the new concentrator and mill started operation. Shortly thereafter it was noted that, despite ponding and treatment of the mine waters and mine waste waters, receiving streams still showed high contents of zinc. It was also observed that a yellowish white, almost colloidal, suspension formed when the treated effluent from the ponds was acidified for the determination of total metal content.

This report details the results of a preliminary investigation of these findings, to ascertain (1) whether the suspension forming in the effluent was interfering with the determination of copper and zinc in the several waters, and (2) whether the high zinc contents found downstream from the mine were inflow of waste effluent from the treatment pond.

Brunswick Mine Operation

Since about June 1964, the high zinc-lead ore from this mining property has been concentrated in a modern flotation plant. Table 1 lists the range of chemicals reported being used in treating Brunswick ore.

TABLE 1

Treatment Chemicals - Brunswick Mill Operation

Chemical	Range (lb/ton of ore)
Aerofloat 242 - a thiosulphate - containing thiocarbonyl	0.02 - 0.15
Reagent 303 - potassium ethyl xanthate	0.05 - 0.2
Dowfroth 250 - a poly propylene glycol ether	0.02 - 0.2
Soda Ash (Na_2CO_3)	0.5 - 5
Lime ($\text{Ca}(\text{OH})_2$)	0.5 - 3

The alkaline tailings or wastes from the concentrator enter a large ponding area where they mix with an acid water pumped directly to the pond from the mine. This mixture is then treated with lime to raise the pH and to precipitate the base metals (copper, zinc and lead). The treated wastes settle in three ponds in series, the overflow from the third pond flowing into the drainage system of the Little River, via the tributary stream, South Little River (see Figure 1).

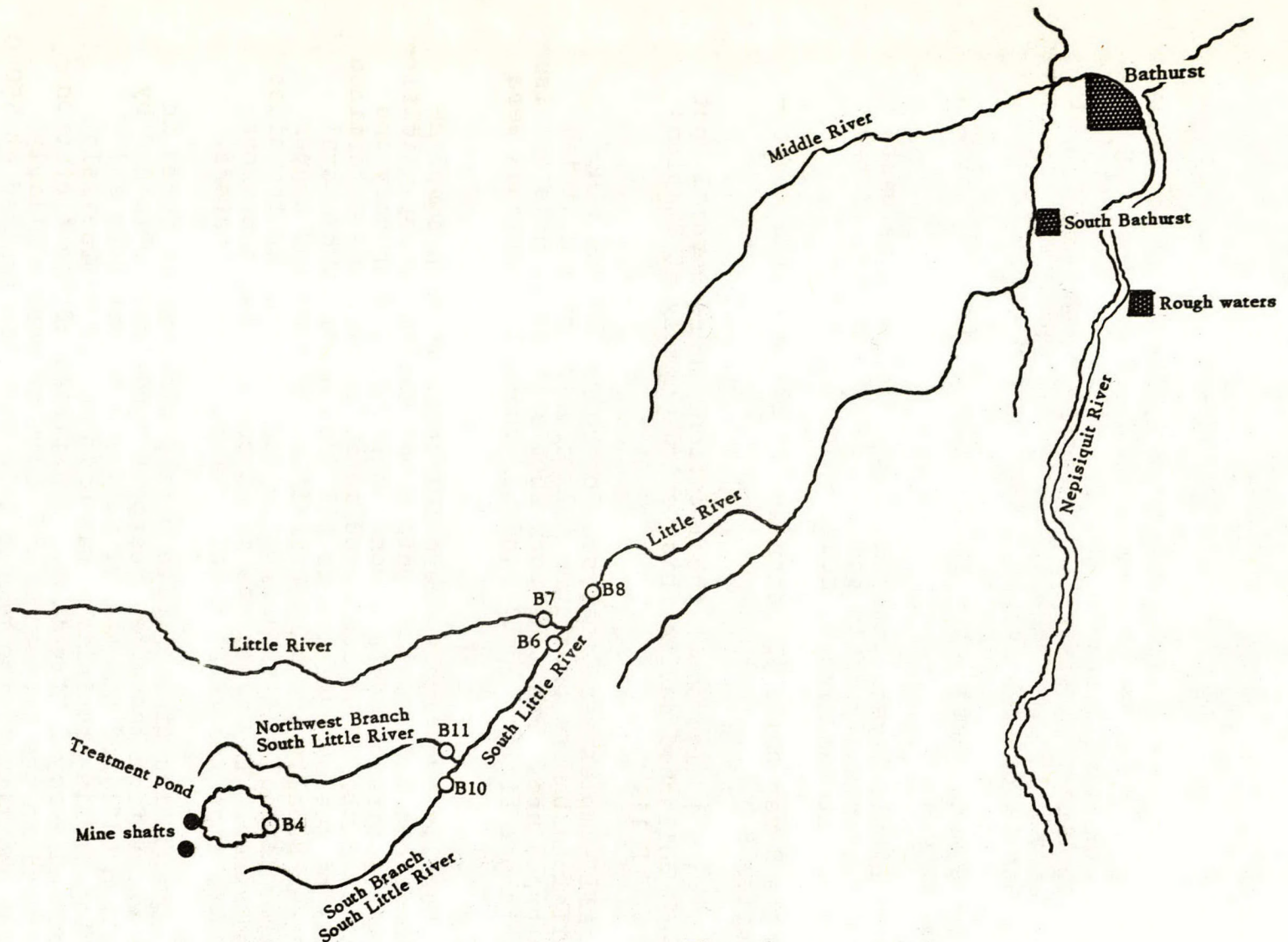


Figure 1
 Brunswick Mine Water Sampling Stations
 Scale 1" = 2 miles

PROCEDURE

Personnel of the Department of Fisheries periodically collected samples from the pond overflow and from receiving streams at the Brunswick mine property. Early in November 1964, a biweekly sampling program was initiated to check the high zinc contents already noted in the Little River; samples were collected at the following locations over a 3-week period (see Figure 1):-

- (i) Treated mine waste water at the outfall from pond No. 3 - Station B 4
- (ii) South Little River, into which the treated mine waste waters eventually drain and below the junction of two branches at the river's mouth - Station B 6
- (iii) Little River below the entrance of South Little River - Station B 8

Figure 1 also shows the locations where several spot samples were collected during this period, namely at Stations B 7, B 10 and B 11.

All samples were analysed for copper by the zinc dibenzylidithiocarbamate procedure and for zinc by a modified dithizone procedure. Previous work showed these methods precise to the parts per billion (ppb) range if special techniques were used.

Usually two samples were collected at each sampling at each location; total metal content was determined by acidification of the entire contents of one container. When only one sample was available, the dissolved metal content was determined by analysis of the supernatant or filtered water. The total metal content usually includes quantities of zinc and copper present as colloidal matter and/or metals adsorbed on the sides of the container. The dissolved metal content is, therefore, usually lower than the total metal content in these waters.

Quantities of the white precipitate, which forms in the waste water from the mine treatment pond, were obtained by acidification (HCl) of the water, followed by settling and centrifuging. This precipitate was examined by ultra-violet absorption and X-ray diffraction. Quantities of the flotation chemicals used in the Brunswick concentrator were similarly examined. A quantity of the precipitate was also ignited at 550°C and the loss on ignition determined; this test is to some extent a measure of the organic content.

To determine whether this precipitated matter interfered in the analytical determinations for zinc and copper or was a

complex containing these metals, quantities of the precipitate were added to standard copper and zinc solutions and to waste waters; also, known amounts of copper and zinc were added to samples of the waste containing the matter. A quantity of the waste water was also evaporated to dryness and ignited at 550°C, the residue was dissolved in acid and analysed for copper and zinc to determine the amount of metal, if any, combined with organic matter lost on ignition, in the precipitate or adsorbed on the precipitate. An aliquot of the waste water was also digested with perchloric acid to destroy organic matter, and was analysed for copper, lead and zinc to be sure that metal was not lost during the destruction of organic matter by ignition at 550°C.

RESULTS AND DISCUSSION

Nature of Precipitate and Possible Interference in Analyses

Table 2 shows that the addition of the precipitate which forms on acidification of the waste effluent does not interfere with recovery of known amounts of added copper or zinc; this is true whether the precipitate is added to standard solutions of copper or zinc or whether known amounts of the metals are added to waste water containing the precipitating matter.

Table 3 confirms previous findings that considerable quantities of copper and zinc, especially the latter, are not detected by analysis of the supernatant or settled samples, i.e., metal is present in the samples as colloidal suspension and/or adsorbed on the container walls.

TABLE 2

Recovery of Copper and Zinc from Waste Waters

<u>Initial Sample</u>	<u>Added</u>	<u>Found</u>	
		Copper ppb	Zinc ppb
Standard Water (0.0 ppb Cu)	quantity of precipitate from waste effluent	3	
" " (0.0 ppb Zn)	" " "		2
" " (50 ppb Cu)	" " "	53	
" " (20 ppb Zn)	" " "		20
" " (60 ppb Cu)	" " "	58	
Waste effluent of Nov. 6/64 - as received	- - -	-	3
Waste effluent, Nov. 6/64 (25 ppb Cu)	50 ppb Cu	76	
" " " (3 ppb Zn)	40 " Zn		40
" " Nov. 10/64 as received	- - -		3
" " " (3 ppb Zn)	40 ppb Zn		42
" " Nov. 13/64 as received	- - -		2
" " " (2 ppb Zn)	40 ppb Zn		40

TABLE 3

Dissolved and Total Metal Content of Treated Waste Waters

Waste Effluents (Station B4)	Copper ppb		Zinc ppb		Lead ppb	
	Diss.	Total	Diss.	Total	Diss.	Total
Sampled Nov. 6/64	25	35	6	33	-	-
" " " (ignited 550°C)		6		40		
" " 10/64	26	39	6	24	-	-
" " 13/64	18	30	4	12	-	-
" " 24/64	7	-	2	-	2200	
" " (After HClO ₄ digestion)		32		8		2600

The results of evaporation of a waste water (sample of November 6, 1964, Table 3) followed by ignition at 550° show possible loss of copper. However, this test was carried out to show whether appreciable metal was present in the precipitate and no special care was taken to remove all metal from the crucible, etc.

A relatively large quantity of lead was found present in the one waste water sample analysed.

Ultra-violet absorption and X-ray diffraction analyses of the precipitated matter indicate that it was organic in nature; its UV-absorption curve showed peak absorption at 215 mμ but did not match the curves of any of the flotation chemicals or one random mixture of these chemicals. The precipitate was completely lost on ignition at 550°C, further evidence of its organic nature. Studies to date have not identified this precipitate.

TABLE 4
Analysis of Mine Waste Waters and Receiving Stream Waters - Brunswick Mine

Source	Sampling Point	Date Sampled	Storage (Days)	Appearance	pH		Specific Conductance (Microhm/cm @ 25°C)	Total Hardness ppm as CaCO ₃	Copper, ppb		Zinc, ppb		Level (ft)	Discharge (cfs)	Ratio Zinc:Copper	
					Lab.	Field			Diss.	Total	Diss.	Total				
Brunswick Mine water	Direct from mine	30-5-64 24-9-64 24-9-64	85 13		3.2 5.0		515 348	53 128		20 79 14		3,900 11,700 6,300		1	195 148 480	
	At outfall to ponds	31-7-64 27-9-64	4 5	Turbid	6.0	11 8.6	1,320	327		41 24		1,600 3,560			39 140	
Brunswick Mine water and tailings mixture	At outfall from third treatment pond - Station B4	31-7-64 27-9-64	59 5			7.6 8.6				97 63		950 18			9.8 0.69	
		6-11-64 10-11-64	6 10	Sl. turbid "	7.0 6.2	7.6 9.0	1,684 1,684	237	25 26		6 6				0.23 0.23	
		13-11-64 17-11-64	7 3	Clear Sl. turbid	8.3 7.9	9.1 10-11	1,649 1,666		18 23		4 4		0.25 0.50	4 7	0.21 0.17	
		20-11-64 24-11-64	16 7	Clear "	10 10.9	10.7 11	1,672 1,718		12 7		7 2		0.3 0.35	5 3.2	0.58 0.29	
		8-6-63 15-6-63	19 8	Brown tint "	6.7 6.9	6.6 7.0	30.4 30.1	11 12			8 1		90 70			
		8-9-63 14-9-63	22 16	Clear "	6.8 6.2	7.0 7.0	47.2 50.3	14 14			1 1		117 139	1.55 1.95		
		21-9-63 29-9-63	9 10	Brown tint Clear	6.6 6.6	6.6 6.6	36.5 62.0	16 17			1 6		142 172	1.3 1.0	21.6	37.6
		5-10-63 12-10-63	12 13	Brown Tint Muddy	6.3 6.3	6.4 6.4	53.0 49.8	15 13.5			1 4		152 164	1.60 1.30	64.8 40.1	21.6
19-10-63 27-10-63	6 5	" Clear	6.4 6.7	6.4 6.6	62 64	17 17			4 5		138 235	1.10 2.70	116.5	47		
3-11-63 10-11-63	5 16	Turbid "	5.9 6.1	6.0 6.4	45.3 46.3	12 13			3 3		178 211	2.0 1.45	108	57		
17-11-63 24-11-63	9 9	" Grey color	6.2 6.9	6.6 6.2	50.1 64.7	14.5 15			0 2		257 228	1.40 2.20	50.4	105		
1-12-63 8-12-63	15 8	Turbid Clear	6.0 6.2	6.0 6.2	45.5 64.5	12 17			2 0		228 250	2.20 -	95	114		
													ice	-		
		8-6-64 11-6-64	5 5	Clear "	6.3 5.9	6.4 6.2	122 76.2	35 23		35 35		32 24			0.92 0.69	
		17-6-64 22-6-64	7 7	Grey color Clear	6.1 5.8	6.3 6.5	114 170	39 57		1 24						
		27-6-64 6-7-64	3 6	Sl. turbid "	8.8 5.6	6.4 6.2	202 283	65 84		4 1		196 117	1.02 1.08	20	196	
		12-7-64 19-7-64	6 6	" Clear	4.4 5.0	6.0 6.0	330 435	104 143		1 3		117 146	0.90	26	117	
		24-7-64 31-7-64	4 4	" "	4.4 4.4	6.0 6.0	435 844	172 249		1 2		208 300	-	15.4	49	
		3-8-64 10-8-64	4 2	" "	4.3 4.1	6.0 6.0	733 933	240 275		28 7		258 223	- 1.10	18.0	75	
		13-8-64 4-9-64	1 11	" "	4.3 3.6	5.0 6.1	929 1,360	360 300		8 4		247 640	1.15 1.9	20.7	31	
		17-9-64 25-10-64	15 8	" "	3.9 3.5	6.0 6.0	1,407 1,026	317 199		8 6		688 450	0.90 1.25	10.0	86	
		6-11-64 10-11-64	6 10	" "	3.4 3.4	34 34	1,115 1,071	195	11 6		490 650	1.00 0.90	-	49		
		13-11-64 17-11-64	7 3	" "	3.5 3.5	3.9 4.4	990 1,112		12 7		760 700	0.95 1.20	10	108		
		20-11-64 24-11-64	10 7	" "	3.3 3.5	3.5 3.6	1,384 1,397		8 10		420 390	1.30 1.25	14	60		
													ice	100		
													ice	52.5		
													ice	39		
Little River	Below junction of South Little River Station B8 (Cage 2B)	13-8-64	1	Clear	4.6	5.0	691	200		3		184	1.35	89	61	
		18-8-64	27	"	5.0	6.1	701	194		0		770	1.15	29.3	-	
		27-8-64	19	"	5.0	6.0	696	184		0		600	1.2	45.7	-	
		10-9-64	18	"	5.7	6.0	945	225		1		642	1.1	50.	642	
		17-9-64	15	"	5.3	6.0	809	211		1		578	1.4	35.0	578	
		30-9-64	14	"	5.1	6.0	937	243		0		640	1.4	33.0	-	
		1-11-64	19	"	4.3	6.0	456	94		5		243	2.05	123	49	
		6-11-64	6	"	3.9	3.9	578	111					1.15	-	27	
	10-11-64	10	"	4.0	4.0	583			7		350	1.00	20	50		
	13-11-64	7	"	4.5	5.0	474			4		340	1.00	20	85		
	17-11-64	3	"	4.1	4.8	685			4		360	1.25	ice	90		
	20-11-64	10	"	3.6	3.8	1,008			4		360	1.25	22	90		
	24-11-64	7	"	3.8	4.0	999			8		330	1.25	ice	41.5		
			8-6-64 17-9-64	5 15	Clear "	6.9 7.3	6.9 7.0	34 76	15 30		7 1		0 6	1.85 1.15	42.3 40.	- 6
			13-11-64	7	Clear	7.1	6.9	62			2		0	1.35	8	-
			13-11-64	7	Clear	3.2	3.65	1,118			15		975	1.00	3	65
		13-11-64	7	Clear	3.7	4.1	1,120			5		124	0.65	4	25	

Metal Content of Receiving Stream Waters

Table 4 tabulates the information available on copper and zinc contents of the waste waters and receiving streams at the Brunswick mine. Included in Table 4 are the analyses of the mine tailings and of mine waters prior to lime treatment and settling in the ponds. The analyses of samples collected in the biweekly sampling study (November 6 to November 24, 1964, inclusive) are also included in Table 4.

As expected from the type of ore at the Brunswick mine, the mine water and waste waters are high in zinc in comparison to copper. From the one analysis of lead, it is probable that the lead content in these waters is also high. There is, however, considerable variation in the total copper and zinc contents, as well as in their relative ratios.

The effluent after treatment and settling in the ponds (Station B4) shows a reversal in the ratio of zinc to copper, i.e., present treatment is producing an effluent relatively low in copper and zinc with zinc removal being more efficient than copper removal. Further investigation of lead removal is necessary.

Receiving stream waters at Station B6 and B8, show high zinc contents even before start-up of the mill (about June 1964) and the treatment pond (Table 4). Since the start-up of the concentrator, the total mineralization (specific conductance) and hardness of the South Little River (Station B6) have steadily increased. The zinc content has not increased in proportion. The mineral content of the Little River (Station B8) has increased during the same period. These findings and the continuing decrease in pH of these river waters over the period June to December 1964 are indicative of an unknown inflow into the river system. As expected, analysis of waters at Station B10 and B11 also shows low pH and high zinc contents. However, Little River above the entrance of the South Little River (Station B7) shows little evidence of contamination; this water has a pH of about 7.0, low mineral content (specific conductance) and low hardness and relatively low metal content.

From available flow rates and analyses (Table 4), it was not possible to find a direct relationship between discharge, total mineral content and zinc content at Stations B4, B6 and B8 because data on all possible inflows were not available.

SUMMARY AND RECOMMENDATIONS

Limited tests to date show that the present alkaline treatment-pond effluent probably contains an organic compound, still unidentified, but this matter, which precipitates on acidification, does not significantly affect the analyses for zinc and copper.

The present treatment shows good removal of zinc and copper.

The receiving streams of the Little South River system show very high zinc contamination, which cannot be due to inflow from the treatment-pond. Decreasing pH, increasing mineralization and high zinc contents in these waters (Little South River and Little River downstream) are also evidence of inflow of acid mine waters containing quantities of zinc. The source of these waters is not known but could be drainage from ore dumps, from contaminated springs, from pumped mine water not reaching the ponds, etc.

It is proposed, as soon as conditions permit, to carry out a detailed survey of the area to ascertain the source of this inflow.

If possible, spot samples from the receiving streams should be collected during the winter when stream flows are at their lowest.

The monitoring program should be started prior to spring break-up to ascertain whether run-off from the land decreases or increases the contamination.

In future investigations, determination of lead should be made to ascertain whether the receiving streams are high in this metal.

Studies will continue in an attempt to identify the precipitate that forms in the waste effluent upon acidification.