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of the  
ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 848.

Concentration of Manganese Ore from  
Cowichan Lake, Vancouver Island,  
British Columbia.

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Shipment:

Four sacks of manganese ore, weight 300 pounds, were received on August 5th, 1939, from E. Priest, 6550 Angus Drive, Vancouver, British Columbia. This material was taken from the "Black Prince" mineral claim, now known as the Manganese Group, at Cowichan Lake, British Columbia.

This shipment was forwarded to determine whether



the ore could be concentrated to obtain a marketable product.

Characteristics of the Ore:

Six polished sections were prepared and examined microscopically for the purpose of determining the possibility of grinding the material to free the manganese mineral for concentration.

Gangue -

The sample is highly siliceous. Occasional patches of white to pink translucent gangue are free from metallic minerals; the remainder of the gangue is intimately associated with the manganese mineral, mostly as a very fine-grained admixture with here gangue predominating and containing finely divided manganese mineral and there the latter mineral predominating and containing finely divided gangue. All gradations in proportions of the two minerals are present in different parts of the specimens.

Manganese Mineral -

The metallic manganese mineral appears to be a single species, finely crystalline and often extremely finely divided, some of the smallest grains even approaching the limit of resolution of the microscope (less than 1 micron) (See Figure 1.). The mineral is hard, and is strongly anisotropic. It is therefore probably to be identified as PYROLUSITE ( $MnO_2$ ). It is not identified as the harder but otherwise very similar mineral polianite ( $MnO_2$ ), because its greater hardness may be due to the finely divided admixed gangue.

Conclusions from Microscopic Examination -

A rough quantitative (microscopic) analysis



indicates that the assemblage of pyrolusite and gangue, which is too intimate to be separated for concentration, is of the order of 40 per cent pyrolusite and 60 per cent gangue on the average. By assuming specific gravities of 4.8 for pyrolusite and 2.6 for gangue this gives a figure of about 55 per cent  $MnO_2$  as probably the best concentrate obtainable under perfect conditions of treatment. To obtain this all of the coarse gangue must be removed.

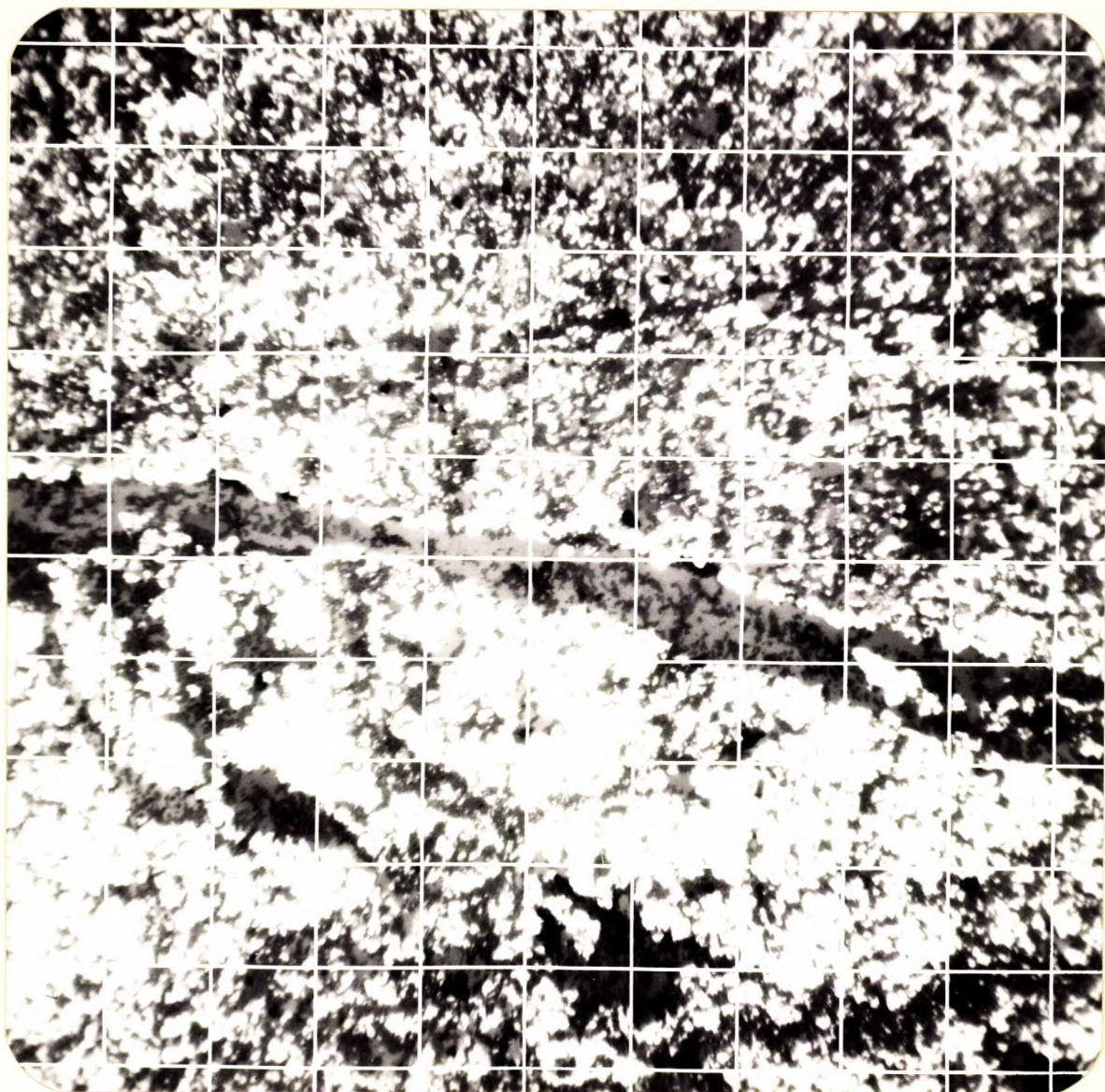
It is to be noted that the above conclusion is based upon the study of polished sections and is only of value in so far as they represent the sample as a whole. It seems probable, however, that they are at least roughly representative, because there does not appear to be any great variation in character. The most probable error would be from selecting material richer in manganese than the sample as a whole.

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(NOTE: Figure 1 is on next page.)



Figure 1.



An average field, showing the intimate admixture of pyrolusite and gangue in a sample from the "Black Prince" mineral claim, Cowichan Lake, British Columbia.

White - pyrolusite; grey - gangue.  
Magnification: X200.  
A 200-mesh screen is superimposed.



Sampling and Analysis:

The sample was crushed, sampled, and analyzed.

Results:

Manganese (Mn)	-	24.89 per cent
Iron (Fe)	-	0.92 "
Sulphur (S)	-	0.30 "
Phosphorus (P)	-	Trace.
Insoluble	-	56.09 per cent.

Investigative Procedure:

Concentration tests made on samples from the "Black Prince" claims in 1919 showed that table concentration was not adaptable.

The present shipment was made to determine if the advances made in metallurgy since that time would have application to the concentration of the ores of this type.

Flotation tests showed that the ore contains pyrolusite, rhodochrosite and rhodonite, the oxide, carbonate and silicates of manganese. This unfavourable distribution of the manganese, together with the physical structure of the ore as shown by the microscopic examination, precludes the production of a high-grade concentrate. One containing approximately 34 per cent manganese may be obtained, with only 50 per cent recovery.

DETAILS OF INVESTIGATIVE TEST WORK:

SECTION I.

From the character of the ore, flotation as applied to non-metallic ores appeared to be the process that offered the most hope of success.

The presence of silicates and oxides suggested



two lines of attack: the first, to float the oxides away from the silicates; and the second, to float the silicates from the oxides.

### Flotation of Oxides.

#### Test No. 1.

In these tests, the anionic reagents, chiefly the soaps, such as oleates, were used.

#### Reagents: (lb./ton)

Soda ash	-	2.0
Sodium silicate	-	0.5
Oleic acid	-	0.25
Sodium oleate	-	0.25
Pine oil	-	0.08

Grind: 53 per cent minus 200 mesh.

pH = 8.4.

#### Results:

Product	<u>Weight,</u>		<u>Assays, per cent</u>		<u>Distribution, per cent</u>	
	: per	:	: Insol-	:	: Insol-	:
	: cent	: Mn	: uble	: Mn	: uble	
Feed (calculated):	100.0	24.94	55.46	100.0	100.0	
Concentrate	: 36.2	34.12	36.52	49.5	23.8	
Cleaner tailing	: 12.2	21.61	62.20	10.5	13.7	
Flotation tailing:	51.6	19.30	67.12	40.0	62.5	

#### Test No. 2.

In this test the grind was increased to 92.4 per cent minus 200 mesh. Other conditions were similar to those in the preceding test.

#### Results:

Product	<u>Weight,</u>		<u>Assays,</u>		<u>Distribution,</u>	
	: per	:	: per cent	:	: per cent	:
	: cent	: Mn	: Insol.	: Mn	: Insol.	
Feed (calculated):	100.0	25.55	55.04	100.0	100.0	
Concentrate	: 25.8	37.00	34.50	37.3	16.2	
Cleaner tailing	: 14.3	27.05	52.40	15.2	13.6	
Flotation tailing:	59.9	20.28	64.50	47.5	70.2	

It is apparent that finer grinding is of no practical advantage.



Test No. 3.

The sodium silicate in this test was raised to 1.0 pound per ton, with the view of decreasing the silica in the concentrate. The grade of concentrate obtained, recoveries, and mineral content of the flotation tailing were practically identical with those of Test No. 1.

Flotation in acid circuit with oleic acid and pine oil as flotation agents produced a concentrate containing 28.5 per cent manganese. There was 17.8 per cent manganese in the tailing.

Test No. 4.

Additional tests with varying technique produced concentrates that were essentially the oxide, the carbonate and the silicate. These had the following analysis:

<u>Concentrate No.</u>	<u>Assay, per cent</u>	
	<u>Mn</u>	<u>CO<sub>2</sub></u>
No. 1	32.02	3.82
No. 2	33.24	12.60
No. 3	19.60	2.06

Flotation of Silicates.

Tests made with cationic reagents in an attempt to float the silicates from the oxides produced low-grade, impure concentrates. Microscopic examination of the products showed that no effective separation had been obtained.



Conclusions from Section I of Test Work:

The results of the first section of the investigation show no indication of the possibility of effecting a concentration of the manganese to obtain a product of commercial grade. This is caused primarily by the structure of the ore, which is an intimate mixture of mineral and gangue.

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SECTION II.

Chemical or Hydrometallurgical Investigation.

Direct metallurgical treatment to the purpose of producing mangano-silicon, silico-manganese, speigeleisen or such, while theoretically possible, would appear to be a doubtful solution from an economic standpoint.

Recently interest has developed in the chemical or hydrometallurgical treatment of low-grade manganese ores and while it can hardly be expected that hydrometallurgy can compete with pyrometallurgy on an equal footing with respect to raw material, the hydrometallurgical process could have an application as a stand-by or a special product process under favourable conditions.

Two processes have been suggested in this field and the details have been fairly well worked out for (1) production of manganese dioxide and (2) manganese metal. Both processes are of the electrolytic type, using aqueous solutions of manganese sulphate in an



electrolytic cell. The first process, without diaphragms, produces  $MnO_2$ ; the second, with diaphragms, produces metallic manganese.

Since electrolysis is involved, the main prerequisite would be cheap electric power. Other factors would involve a supply of cheap solvent (sulphuric acid and ammonium sulphate) and cheap fuel or natural gas.

In view of the interest in and possibilities of a hydrometallurgical treatment method of utilizing the Cowichan manganese ore, this laboratory conducted a few tests of a preliminary character along this line. The following is a brief summary of the tests performed and the results obtained.

The solvents generally recognized as being commercially applicable to leaching manganese oxides from ores are: (a) ammonium sulphate ( $NH_4SO_4$ ), (b) sulphurous acid ( $SO_2H_2O$ ), and (c) sulphuric acid ( $H_2SO_4$ ).

Solvents (a) and (c) are employed for ores which contain manganese in manganous condition, such as Rhodochrosite ( $MnCO_3$ ). Ores of the higher oxide type, pyrolusite, psilomelane, etc., are amenable to leaching with sulphurous acid. Ores of the latter type, composed of  $MnO_2$  or  $Mn_2O_3$ , however, can be subjected to reduction by heating in a reducing atmosphere to form manganous oxide ( $MnO$ ) which compound is soluble in solvents (a) and (c) but not soluble in sulphurous acid ( $SO_2-H_2O$ ).

The manganese in the Cowichan Lake ores is principally rhodonite, a manganous silicate.

This mineral has been considered to be the



most difficult of any of the manganese minerals to treat by chemical means.

The results of our tests, however, indicate that the manganese can be almost completely removed by a process of reducing roasting and subsequent leaching of the manganous oxide formed.

Results of Tests:

Numerous tests were conducted by leaching the raw ore with the above-mentioned solvents.

Ammonium sulphate extracted a maximum of 4.5 per cent of the manganese, which amount is probably present mostly as rhodochrosite. The grind was 62.7 per cent minus 200 mesh.

Sulphurous acid extracted a maximum of approximately 50 per cent of the manganese in a 2-hour leach at the same grind. This would indicate the presence of some higher oxides of manganese in the ore, but probably not to the extent indicated by the extraction, as secondary reactions most likely are involved.

Sulphuric acid showed an extraction of 35 per cent of the manganese in one hour, a result more or less expected in view of the fact that the manganese is considered to be present in the lower oxide form.

Sulphuric Acid and Sulphurous Acid -

In view of the extraction results obtained by these two solvents separately and the possibility of the presence of both the lower and higher oxides, a test was conducted using both solvents. The highest extraction was obtained by leaching first with 10 per cent sulphuric acid, filtering and repulping the insoluble residue in saturated sulphurous acid, and leaching for one hour.

(Continued on next page)



The total extraction was 70 per cent of the manganese. The difference between the total extraction and the sum of the two separate extractions is probably due to secondary reactions.

#### Oxidizing Roasting Prior to Leaching.

It has been demonstrated by other investigators that an oxidizing roast carried out at 750° C. has had the effect of altering some manganese oxides and making them more amenable to solvent extraction. Several tests were conducted along this line, but the results were quite unsatisfactory.

#### Reducing Roasting Prior to Leaching.

The reduction of higher oxides of manganese to the monoxide form has long been known but has not had much practical application.

In 1937 the U. S. Bureau of Mines started an investigation for the utilization of low-grade manganese ores of the higher oxide type, using this principle of first producing the monoxide and then leaching with sulphuric acid. This work was carried through and resulted in the development of a process, known as the Shelton process, for electrolytic production of metallic manganese.

In brief the process consists of heating the ore in a highly reducing gas atmosphere, such as natural gas, coal gas or producer gas, with precautions for keeping the discharging reduced ore under a reducing atmosphere until cold.

The reduced ore is then leached with a mixture



of sulphuric acid and ammonium sulphate, the solution extract purified of iron and other impurities, and the pure manganous sulphate solution thus obtained subjected to electrolysis in a diaphragm cell. Metallic manganese is thus produced and the acid regenerated in the cell for further leaching.

This process is under large-scale test operation at present in Knoxville, Tennessee.

Description of Our Test Work:

In our test work, 200-gramme samples of ore at minus 14 mesh were placed in small retorts, the retorts being placed in a muffle furnace and heated to 1500° to 1560° F. with a stream of city gas passing through the retorts. Finer mesh material reduced slightly quicker than coarse mesh, but reduction appeared complete in one to two hours.

The retorts were allowed to cool down with a slow current of gas passing through them to prevent any re-oxidation of oxide.

Portions of the reduced material were leached with 10 per cent sulphuric acid; or 5 per cent sulphuric acid and 20 per cent ammonium sulphate; or with ammonium sulphate alone.

The ammonium sulphate extracted about 40 per cent of the manganese with evolution of ammonia. This result was disappointing, as it was hoped a procedure might be worked out to simply leach with ammonium sulphate producing manganous sulphate and then use the ammonia set free in the reaction to precipitate a



high-grade manganese oxide from the manganous sulphate solution and regenerate ammonium sulphate. However, as stated, the results were not satisfactory as to recovery.

Sulphuric acid completely leached the manganese from the reduced ore in one hour.

Sulphuric acid plus ammonium sulphate, which forms the electrolyte of the Shelton process, likewise completely extracted the manganese from the reduced ore.

These results are somewhat surprising in view of the consensus of opinion among other investigators that rhodonite was difficult to treat by such a scheme as outlined above. However, several tests were conducted on this material and first results corroborated.

#### Electrolysis of Manganous Sulphate.

Electrolytic separation of the manganese was not attempted in this test work. This phase of the process is fairly well established except in the matter of impurities in the electrolyte and their effect on deposition.

The manganese in the sulphate solution may be recovered either as manganese dioxide, suitable for dry cell batteries, ceramic and other uses, or as metallic manganese.

Experiments have indicated that for  $MnO_2$  production the power consumption for electrolysis would be around 2,000 K.W.H. per pound and for the metallic



electrolytic manganese production, around 3,500 K.W.H. per pound.

Gas for reduction of the oxides can readily be produced from any sort of fuel, wood, coal or oil, and its cost will depend on its availability to site of operations.

The chemicals, outside of a few which may be necessary for the purpose of electrolyte purification, are principally sulphuric acid and ammonium sulphate, and as these are regenerated in the electrolysis, additional acid will only be required to take care of losses through leaks, washing, etc. Such loss should be comparatively low.

The reports of the U. S. Bureau of Mines describe the process in detail and should be referred to for fuller information. The following reports are recommended for study:

- R. I. 3357, December 1937, page 19.
- R. I. 3406, July 1938, page 3.
- R. I. 3419, October 1938, page 13.

Shawinigan Chemicals Limited, at Shawinigan Falls, Quebec, have an arrangement for the rights of this process in Canada.

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