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Beneficiation Studies of the Low-Grade Skarn Phosphate from Mactung Tungsten Deposit, Yukon, Canada

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Abstract: A preliminary beneficiation study of low-grade skarn phosphate rocks from Mactung tungsten deposit, along the Yukon and Northwest Territories border in Canada, was carried out through standard Bond Work Index, grinding test and laboratory batch flotation tests. The skarn phosphate sample assayed 12.65% P_2O_5 (about 30% apatite), 31.71% CaO and 35.46% SiO_2. The main gangue minerals included calcite, quartz, calc-silicates, amphibole, feldspar, and pyrrhotite. The sample had a Bond Work Index of 19.04 kWh/t, belonging to a hard ore category. The beneficiation study of the skarn phosphate sample was carried out using "direct–reverse flotation" method. The direct flotation was carried out using sodium carbonate, sodium silicate solution (water glass) and sodium oleate. Sulfuric acid and phosphoric acid were used in the reverse flotation of the carbonate gangue. One phosphorous rougher flotation, one bulk cleaner flotation and one carbonate reverse flotation at ore grind size of 86% passing 53 μm led to a phosphate concentrate assaying 28.68% P_2O_5, 12.06% SiO_2, 0.72% MgO and 46.98% CaO, at a P_2O_5 recovery of 70.9%.

Keywords: skarn phosphate; Mactung tungsten deposit; direct-reverse flotation; sodium oleate; phosphoric acid; sulfuric acid

1. Introduction

Phosphorous (P), located in the 15th position of the periodic table, is one of the most indispensable non-metal elements in life. Its oxidized form, phosphates (PO_4^{3-}), plays essential roles in DNA, RNA and ATP structural building, which are vitally important for the growth and development of each and every organism on the planet Earth [?]. One of the principal industrial applications of phosphorous is the manufacture of fertilizer for the agricultural sector [?]. As it cannot be replaced by other nutritional elements in plant growth, phosphorous is an essential component of global food security and related world affairs [?]. As a result, phosphate minerals have been recognized as a critical and strategic natural resource by the European Union and United States [? ?].

Phosphorous occurs naturally as phosphate due to its high reactivity [?]. Its natural sources include igneous apatite, sedimentary phosphorite, biogenic, and their weathering residuum [? ?]. Sedimentary phosphorite accounts for over 80% of global production while the remainder comes from igneous rocks and other subordinate sources [?]. According to the U.S. Geological Survey, although there are no imminent shortages of phosphate rocks globally, the high-grade and easy-to-process phosphate reserves are highly segregated geographically [?]. For example, Morocco and its occupied Western Sahara alone controls about 71% share of phosphate reserves. This is followed by China, Algeria, Syria, Brazil, South Africa and Saudi Arabia, which account collectively for 17% global phosphate reserves. Such an uneven distribution of such a critical resource could pose significant risks and uncertainties to other countries. Canada has a few known phosphate deposits and occurrences, including Lac à Paul, Wapiti, Fernie, and Mactung [?]. Although recognized as one of the largest agriculture producers and a top fertilizer manufacturer,

Canada has been depending solely on imports of phosphate rocks from other countries after the only operating phosphate mine in Kapuskasing was shut down in 2013 [? ?]. To secure a domestic supply chain of phosphorous for her fertilizer industry, this paper describes a study of a phosphate mineralization spatially associated with the Mactung tungsten deposit.

The Mactung tungsten deposit is geographically located at latitude 63°17′ N and longitude130°10′ W, in the Selwyn Mountain Range, along the Yukon/Northwest Territories border. It is one of the world's largest tungsten deposits, with an estimated indicated mineral resource of 33.0 Mt grading 0.88% WO_3 and 11.9 Mt grading 0.78% WO_3 in the inferred category [?]. The current mine plan targets the extraction of only scheelite-hosted tungsten, with no plan of processing the associated phosphate. The phosphate mineralization in Mactung is of sedimentary origin, formed by the precipitation of apatite from phosphorus rich water, mediated by microbial activity. The mineralization consists of nodular breccia clasts of cryptocrystalline apatite ("collophane") in a limestone unit known as Unit 3D (highlighted in Figure ??). The phosphate mineralization spatially overlaps and extends beyond the skarn tungsten deposit. More than 50 million tons of phosphate resources grading at 10 wt% P_2O_5 on average has been estimated in Unit 3D within a 4 km^2 area around the tungsten deposit.
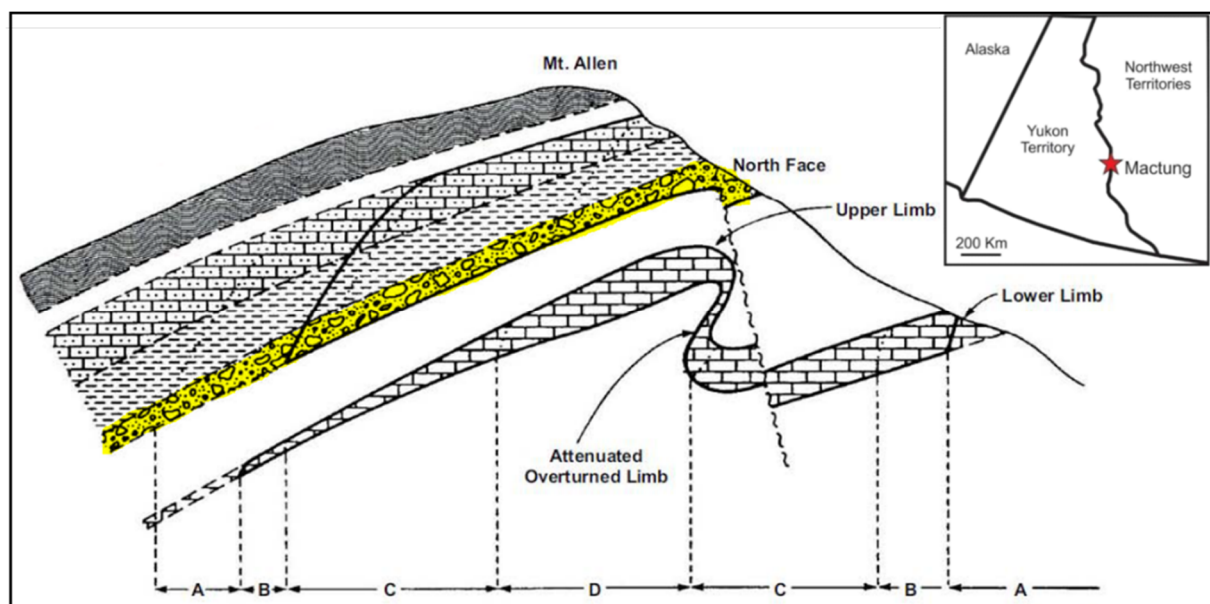
Figure 1. The stratigraphic sequence of phosphate (Unit 3D, highlighted) on the N-S cross section of the Mactung skarn deposit. Figure was modified from [?].

The phosphate coinciding spatially with the skarn tungsten deposit was thermally and metasomatically altered by subjacent Cambrian to Devonian igneous intrusions that formed the tungsten deposit; and it is thus referred to as skarn phosphate and is the focus of this study. Unlike typical sedimentary phosphorite that are associated mainly with sedimentary carbonate minerals, skarn phosphate deposits contain significant non-carbonate minerals with diverse textures [?]. The alteration of the phosphorite in Mactung resulted in the recrystallization of both the phosphate and carbonate minerals as well as the introduction of new mineral phases including calc-silicates and sulfides [?]. The challenges associated with the presence of these 'exotic' mineral phases are probably some of the key reasons the mine is not envisaging processing the phosphorite even though it would be mined together with the tungsten ore. This makes the study interesting both scientifically and economically.

Retaining the phosphate in the mine tailings, however, could result in future environmental liabilities from any leakage into the aquatic ecosystem. Although hydroxyapatite

is considered the most stable phosphate salt under most conditions in nature, its solubility can be significantly enhanced by acid mine drainage from the supergene oxidative breakdown of iron sulfides in the tailings [**?**]. The presence of enhanced phosphorous concentration in drainage systems has been associated with many negative environmental impacts including eutrophication of lakes and algae bloom that may cause fish die-offs, which is strictly prohibited by environmental regulations [**?**]. In addition, the current mineral beneficiation infrastructures setup for the tungsten concentration at Mactung could substantially reduce the financial cost for phosphate project. Flotation reagents, such as fatty acids, soda ash, sodium silicate and frother, which are used in scheelite flotation can be used in phosphate flotation as well [**?** **?** **?**]. Therefore, it is necessary to develop a management plan for phosphate at Mactung property, which could involve phosphate ore processing for downstream industrial applications.

Flotation is the common technique widely used in the industry for the beneficiation of phosphate rock [**?**]. Based on the types of collectors (anionic fatty acids or cationic amines) used in the process, the phosphate flotation techniques can be divided into (1) all-cationic flotation [**?**]; (2) all-anionic flotation [**?**] and (3) cationic-anionic (or anionic-cationic) flotation [**?** **?** **?**]. These flotation methods were technically known, respectively, as direct flotation, reverse flotation, direct-reverse flotation or reverse-direct flotation, depending on the types of ores and nature of gangue minerals [**?**]. Direct and reverse flotation processes have been successfully applied in the beneficiation of siliceous and calcareous phosphate rocks, respectively [**?**]. A direct-reverse flotation process has been suggested for low-grade phosphate rocks containing both silicate and carbonate gangue minerals [**?**]. In this process, the first step is designed to float as much phosphate as possible using anionic fatty acid salts as a collector, with the slurry pH maintained at 9–10 using soda ash, and water glass as a silicate depressant. In the second step, i.e., reverse flotation, carbonate gangues (mostly calcite and/or dolomite) is selectively floated off the phosphate concentrate from the first stage to obtain a qualified final phosphate product [**?**]. Although the separation efficiency has been a scientific challenge due to their similar physiochemical properties [**?** **?** **?**], research has shown that slightly acidic conditions adjusted by combined sulfuric acid and phosphoric acid could enhance the flotation efficiency [**?** **?** **?** **?**].

The aim of the current study was to examine the feasibility of beneficiating the skarn phosphate mineralization associated with Mactung tungsten deposit into a concentrate that could be used to manufacture fertilizer (>30% P_2O_5, $CaO/P_2O_5 < 1.6$, and $MgO < 1\%$). Given the low-grade nature of the ore and its mineralogical composition, a flowsheet comprising both direct and reverse flotation was used. Other parameters evaluated include the Bond Work Index, grinding test and mineralogical composition.

2. Materials and Methods

2.1. Ore Samples

A composite skarn phosphate rock sample was collected from cores of drill holes MS164 and MS211 that intercepted mine Unit 3D containing skarn phosphate mineralization. The samples were selected based on assay results from prior exploration programs and visual observation because phosphatic clasts are visible on cores and outcrops (Figure **??**). The sample was crushed in a Retsch model BB200 laboratory jaw crusher to −6 mesh (−3.35 mm), riffled into 500-g charges and stored in sealed plastic bags for beneficiation and analysis.

Figure 2. Photograph of core sample of Unit 3D showing greenish grey skarn phosphate clasts in a whitish grey carbonate matrix.

2.2. Reagents

Sodium oleate (NaOl; ≥82% oleic acid basis) was purchased from Sigma-Aldrich (Saint Louis, MO, USA) and was used as an anionic collector in the phosphate flotation without any further purification. Potassium amyl xanthate (PAX) at 80% purity was obtained from Prospec Chemicals (Fort Saskatchewan, AB, Canada) and was used as a sulfide mineral collector to remove sulfide minerals. Methyl isobutyl carbinol (MIBC) bought from Sigma-Aldrich was also used as a frother in sulfide flotation stage. Sodium silicate solution (water glass) with a modulus of 1.82 from Sigma-Aldrich was used to depress quartz and silicate minerals. Analytical grade sodium carbonate, sulfuric acid and phosphoric acid were purchased from Fisher Chemical (Waltham MA, USA) and used to adjust the pulp pH.

2.3. Bond Work Index

The Bond Work Index (grindability) of skarn phosphate rock sample was determined in a laboratory $8'' \times 8''$ ball mill using a 100 mesh (150 μm) test sieve, with proper scaling factors for the standard $12'' \times 12''$ ball mill.

The Bond Work Index was calculated using the following equation:

$$Wi = \frac{4.45}{P_1^{0.23}(f \cdot G)^{0.82}\left(\frac{1}{\sqrt{P}} - \frac{1}{\sqrt{F}}\right)} \tag{1}$$

where W_i is the Bond Work Index for a given material (kWh/t); P_1 is the test sieve opening size in μm; F is the size in μm at which 80% of feed passes; P is the size in μm at which 80% of the last cycle sieve undersize product passes; f is the scale up factor from $8'' \times 8''$ to a standard $12'' \times 12''$ ball mill, $f = \left(\frac{12}{8}\right)^3 = 3.375$. G is the ball mill grindability (gram/revolution), which was averaged from the last three grinding cycles (equilibrium grinding condition) to simulate 250% circulation load, at equilibrium grinding condi-

tion. The equilibrium condition was usually achieved after 6–12 cycles until a constant grindability value was reached.

2.4. Grinding

A grinding test was carried out using a Titan 8 × 16-inch stainless steel laboratory rod mill, with 24 stainless steel rods of various diameters having a total weight of 15.8 kg. The phosphate rock sample was ground in batches of 500 g with 200 mL of tap water. A slurry was washed into a 1.5 L flotation tank with 800 mL tap water after grinding for 2, 4, 6, and 7 min, and agitated at 800 rpm. About 100 mL sample of each slurry was wet sieved using 140, 200, 325, 400 mesh sieves (105 μm, 75 μm, 45 μm and 38 μm, respectively) to obtain the grind size distribution.

2.5. Froth Flotation

The phosphate rock sample was subjected to a direct flotation step followed by a reverse flotation step in a Denver D-12 laboratory flotation machine with a 1.5 L stainless steel flotation cell. A schematic flowsheet of the flotation process is shown in Figure **??**. In each flotation test, 500 g of sample were added together with 1 L tap water, and operated at 800 rpm impeller speed and 3 L/min aeration rate during the flotation scraping. The first step in the flotation was the removal of sulfide minerals using potassium amyl xanthate (PAX) as a collector. This was followed by the direct flotation of apatite and carbonate minerals in alkaline condition using an anionic sodium oleate collector and water glass as a quartz/silicate depressant. Subsequently, a reverse flotation step was carried out on the direct flotation concentrate to float carbonate gangue minerals in acidic conditions adjusted by sulfuric and phosphoric acids. To acquire a higher P_2O_5 grade in the phosphate concentrate, in some tests, a bulk cleaner flotation was performed after the direct flotation.
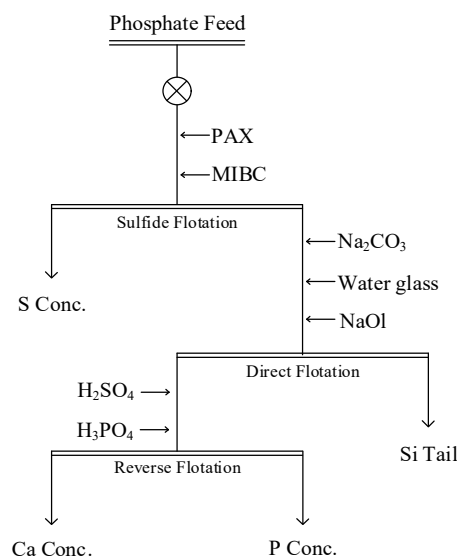
Figure 3. Schematic principle flowsheet of the beneficiation; In some tests, there was an additional cleaning flotation step of the floated phosphate minerals.

2.6. Sample Analysis

A pulverized head sample of the skarn phosphate rocks was analyzed for major elements at Bureau Veritas Commodities Canada Ltd. (Richmond, BC, Canada), a Vancouver-based commercial assay laboratory. The mineralogical composition of the sample was characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV operated at 38 kV, 38 mA and 2 degree/min scan rate at the Department of Earth and Atmospheric Sciences, University of Alberta. The flotation products were analyzed in-house using a Bruker CTX800 countertop X-ray Fluorescence analyzer (Bruker, Kennewick, WA, USA), with

calibration packages provided by Bruker. Samples of selected products were also analyzed at Bureau Veritas Commodities Canada Ltd. The assay results in the text are identified as "XRF" or "BV" to differentiate those analyzed in-house (XRF) from those analyzed at Bureau Veritas Commodities Canada Ltd. (BV).

3. Results

3.1. Sample Characterization

The mineralogical composition of the phosphate rock was characterized by optical microscopy and powder X-ray diffraction (XRD). Collophane, a cryptocrystalline apatite, is found to be the main phosphate mineral. The collophane occurs as poorly sorted, fine to coarse nodular slump breccia clasts with a calcitic limestone-dominated matrix (Figure **??**). The collophane has a greyish to light green color, unlike in the unskarned ore where it is black to bluish-black [**?**]. The sample also contains trace amount of rare earth element Ce that exists in the baddeleyite mineral. Other gangue phases include quartz, pyrrhotite, anorthite, riebeckite magnesio-hastingsite, hedenbergite, and orthoclase (Figure **??**).
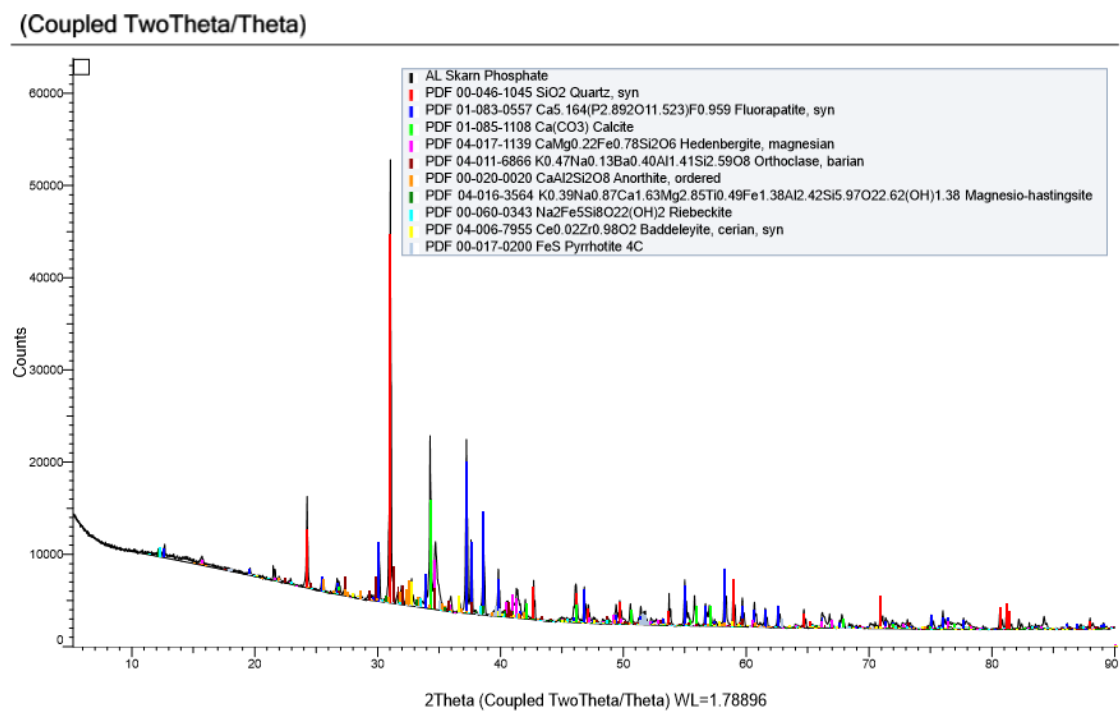

Figure 4. XRD pattern of skarn phosphate sample.

The whole rock major and trace elements composition are shown in Table **??**. The Bond Work Index of the ore is found to be 19.04 kWh/t, which falls in the hard ore category of the ore hardness index [**?**].

Table 1. Whole rock analysis of skarn phosphate (SP) samples.

Component	%
Al_2O_3	3.29
Ba	0.63
CaO	31.71
Cr_2O_3	0.05
Fe_2O_3	6.25
K_2O	0.38
MgO	1.75
Mn_2O	0.34
Na_2O	0.12
P_2O_5	12.65
SO_3	1.679
SiO_2	35.46
Sr	0.023
TiO_2	0.29
LOI *	4.8
Total C	1.75
Total S	0.75

* LOI: Loss on ignition.

3.2. Grinding Test

The grinding tests were carried out with the 8 × 16-inch Titan laboratory rod mill described in Section **??**. After 500 g skarn phosphate and 200 mL tap water were charged into the rod mill, the ore slurry was progressively ground in periods of 2, 4, 6, 7 min. The mill content was then removed and wet screened using 140, 200, 325, 400 mesh sieves (105 μm, 75 μm, 45 μm, and 38 μm), respectively. A relationship between grind time and product size distribution is shown in Figure **??**.
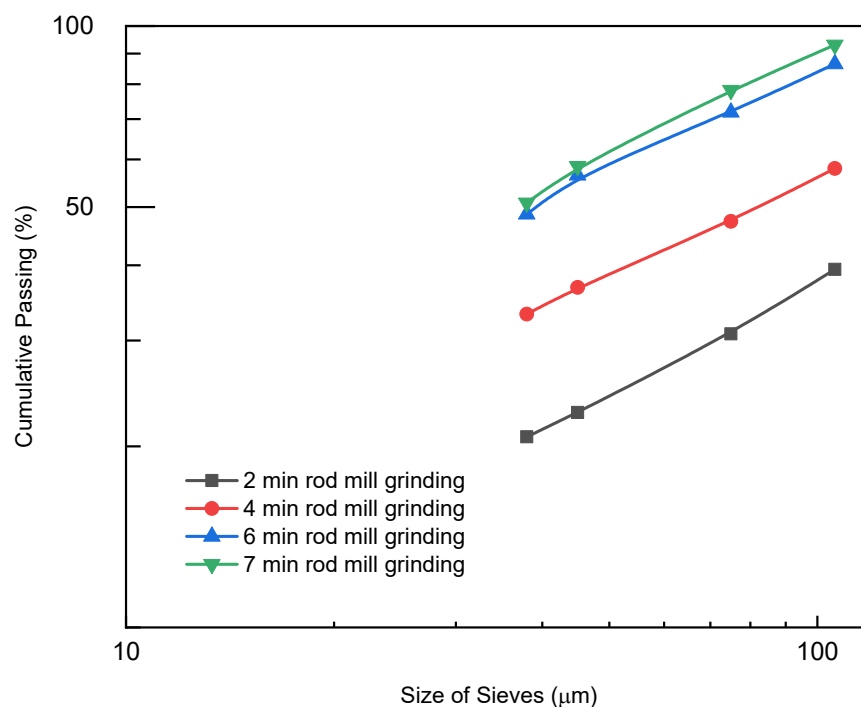
Figure 5. Variation of the cumulative particle size distribution of skarn phosphate sample as a function of grinding time in a Titan rod mill.

3.3. Batch Flotation Tests

The batch flotation of the skarn phosphate rock sample was tested using "direct flotation–reverse flotation" method. The grinding-flotation experiment, reagent dosage optimization in the direct phosphorous flotation and reverse carbonate flotation were investigated.

3.3.1. Effect of Grind Size

The effect of sample grind size on the direct flotation of the skarn phosphate rock sample was carried out. The following reagent dosages were selected based on previous lab experience: 60 g/t potassium amyl xanthate and 40 g/t MIBC were added in sulfide flotation; 4 kg/t sodium carbonate, 3 kg/t sodium silicate solution, 400 g/t sodium oleate were added in the direct phosphate rougher flotation. The results are summarized in Table **??**.

Table 2. The results of grinding-flotation tests on skarn phosphate.

Test #	Grind Size	Products	Weight		Assay (XRF), (%)					Distribution (%)				
			(g)	(%)	P_2O_5	CaO	MgO	SiO_2	SO_3	P_2O_5	CaO	MgO	SiO_2	SO_3
SP-1	78% −106 μm	P Conc	76.9	17.2	18.85	47.00	1.31	6.81	0.15	28.1	25.6	12.1	3.5	1.3
		Si Tail	363.3	81.1	9.98	28.54	1.99	39.19	0.91	70.3	73.5	86.5	95.8	35.7
		S Conc	440.2	98.3	11.53	31.77	1.87	33.54	0.78	98.4	99.1	98.6	99.3	36.9
		S Tail	7.7	1.7	10.64	17.53	1.53	14.14	76.41	1.6	1.0	1.4	0.7	63.1
		Feed	447.8	100.0	11.51	31.52	1.86	33.21	2.07	100.0	100.0	100.0	100.0	100.0
SP-2	75% −53 μm	P Conc	141.5	31.9	20.23	48.90	0.89	8.95	0.00	52.6	48.5	17.9	8.8	0.0
		Si Tail	287.8	64.8	8.33	24.18	1.94	44.66	1.34	44.1	48.8	79.6	89.1	50.8
		S Conc	429.3	96.7	12.25	32.33	1.59	32.89	0.90	96.6	97.3	97.4	97.8	50.8
		S Tail	14.6	3.3	12.55	26.90	1.22	21.57	25.61	3.4	2.8	2.6	2.2	49.2
		Feed	443.9	100.0	12.26	32.15	1.58	32.52	1.71	100.0	100.0	100.0	100.0	100.0
SP-3	86% −53 μm	P Conc	166.3	37.3	20.56	49.47	0.88	9.92	0.00	62.5	57.1	22.8	11.2	0.0
		Si Tail	260.8	58.5	6.91	21.60	1.79	48.52	1.66	33.0	39.1	72.9	85.8	56.7
		S Conc	427.1	95.8	12.23	32.45	1.43	33.49	1.01	95.5	96.2	95.7	97.0	56.7
		S Tail	18.8	4.2	13.12	28.79	1.48	23.82	17.54	4.5	3.8	4.4	3.0	43.3
		Feed	445.9	100.0	12.26	32.30	1.43	33.09	1.71	100.0	100.0	100.0	100.0	100.0

As can be seen, the decrease in grind size of skarn phosphate significantly enhanced the flotation performance at the tested reagent dosages. The best flotation result was observed in test SP-3 with a grind size of 86% passing 53 μm. Further decrease in ore grind size was not tested due to cost-effectiveness consideration. The subsequent batch flotation tests were carried out using the 86% passing 53 μm grind size.

3.3.2. Direct Phosphate Rougher Flotation
The Effect of Sodium Carbonate

The effect of sodium carbonate on the batch flotation of skarn phosphate was tested at a grind size of 86% passing 53 μm. The dosages of sodium silicate and sodium oleate were fixed at 3 kg/t and 400 g/t, respectively. The results are shown in Table **??**.

The best flotation response was achieved through direct flotation of phosphate using 5 kg/t sodium carbonate. The P_2O_5 recovery increased by about 10 percentage points while P_2O_5 grade remained the same (compare SP-3 and SP-4). A further increase in sodium carbonate dosage resulted in a decrease in both P_2O_5 grade and recovery.

The Effect of Sodium Silicate and Sodium Oleate

The optimal dosages of sodium silicate and sodium oleate were determined in batch flotation tests SP-4, SP-6 to SP-8. The detailed flotation reagents and corresponding dosages used in the tests are listed in Table **??** and the flotation results are summarized in Table **??**.

Table 3. The results of phosphate rougher flotation.

Test #	Sodium Carbonate (g/t)	Products	Weight		Assay (XRF), (%)					Distribution (%)				
			(g)	(%)	P$_2$O$_5$	CaO	MgO	SiO$_2$	SO$_3$	P$_2$O$_5$	CaO	MgO	SiO$_2$	SO$_3$
SP-3	4000	P Conc	166.3	37.29	20.56	49.47	0.88	9.92	0.00	62.52	57.12	22.76	11.19	0.00
		Si Tail	260.8	58.49	6.91	21.60	1.79	48.52	1.66	32.97	39.12	72.89	85.78	56.71
		S Tail	427.1	95.79	12.23	32.45	1.43	33.49	1.01	95.49	96.24	95.65	96.97	56.71
SP-4	5000	P Conc	221.2	44.39	20.16	46.63	1.41	11.22	0.00	73.09	66.05	36.84	16.01	0.00
		Si Tail	259.8	52.14	5.43	18.46	1.96	48.46	2.39	23.12	30.70	60.06	81.22	66.87
		S Tail	481.0	96.52	12.20	31.41	1.71	31.33	1.29	96.21	96.75	96.90	97.23	66.87
SP-5	6000	P Conc	198.1	39.54	19.85	47.09	1.21	10.31	0.00	66.35	58.23	31.14	12.55	0.00
		Si Tail	288.9	57.64	6.25	21.72	1.77	48.20	2.51	30.46	39.15	66.21	85.56	71.58
		S Tail	487.0	97.18	11.78	32.04	1.54	32.78	1.49	96.81	97.38	97.35	98.12	71.58

Table 4. The flotation conditions of phosphate rougher flotation of skarn phosphate.

Test #	Sodium Carbonate, g/t	Sodium Silicate, g/t	Sodium Oleate, g/t
SP-4	5000	3000	400
SP-6	5000	3000	600
SP-7	5000	2000	600
SP-8	5000	2000	800

Table 5. The results of direct phosphate flotation.

Test #	Products	Weight		Assay (XRF), (%)					Distribution (%)				
		(g)	(%)	P$_2$O$_5$	CaO	MgO	SiO$_2$	SO$_3$	P$_2$O$_5$	CaO	MgO	SiO$_2$	SO$_3$
SP-4	P Conc	221.2	44.39	20.16	46.63	1.41	11.22	0.00	73.09	66.05	36.84	16.01	0.00
	Si Tail	259.8	52.14	5.43	18.46	1.96	48.46	2.39	23.12	30.70	60.06	81.22	66.87
	S Tail	481.0	96.52	12.20	31.41	1.71	31.33	1.29	96.21	96.75	96.90	97.23	66.87
SP-6	Ca+P Conc1	240.2	48.32	21.55	47.67	0.88	8.94	0.12	80.30	71.37	27.45	14.29	2.83
	Si Tail	241.1	48.50	4.40	17.08	2.24	51.96	2.89	16.45	25.66	70.08	83.37	69.01
	S Tail	481.3	96.83	12.96	32.35	1.56	30.49	1.51	96.75	97.03	97.53	97.66	71.84
SP-7	Ca+P Conc1	249.6	50.52	20.79	45.42	1.37	11.08	0.14	84.72	73.84	40.57	17.65	3.61
	Si Tail	223.6	45.25	2.88	14.93	2.11	55.42	3.14	10.50	21.74	56.09	79.06	72.19
	S Tail	473.2	95.76	12.33	31.01	1.72	32.03	1.56	95.22	95.58	96.66	96.71	75.80
SP-8	Ca+P Conc2	226.3	45.70	23.01	49.44	0.94	8.81	0.33	81.51	70.94	27.43	12.93	6.84
	Si Tail2	42.5	8.58	8.30	22.05	1.83	43.26	1.38	5.52	5.94	10.03	11.91	5.43
	Ca+P Conc1	268.8	54.27	20.68	45.11	1.08	14.25	0.49	87.04	76.87	37.46	24.83	12.27
	Si Tail1	211.6	42.73	2.93	15.02	2.22	53.24	3.49	9.70	20.16	60.56	73.03	68.42
	S Tail	480.4	97.00	12.86	31.86	1.58	31.43	1.81	96.74	97.03	98.02	97.86	80.69

"S Tail" refers to the rejected sulfide concentrate in the 1st stage sulfide flotation; "P Conc" or "Ca+P Conc1" refers to the carbonate concentrate of the rougher phosphate flotation stage; "Si Tail" or "Si Tail1" refers to the tailings of the rougher phosphate flotation stage; "Ca+P Conc2" refers to the carbonate concentrate of the bulk phosphate flotation stage after rougher phosphate flotation stage; "Si Tail2" refers to the silicate tailings of the bulk phosphate flotation stage after rougher phosphate flotation stage.

As can be seen in Table **??**, 400 g/t sodium oleate was not sufficient in collecting the phosphate mineral. The P$_2$O$_5$ recovery was increased from 73% to 80% and the P$_2$O$_5$ grade from 20.16% to 21.55% when sodium oleate dosage was increased from 400 g/t to 600 g/t (compare SP-4 and SP-6). When the dosage of sodium silicate was decreased from 3 kg/t to 2 kg/t (compare SP-6 and SP-7), the P$_2$O$_5$ grade of froth concentrate decreased slightly by about 1 percentage point, but the P$_2$O$_5$ recovery increased by four percentage points. Therefore 2 kg/t sodium silicate was a suitable dosage as the silicate depressant used in the flotation. Further increase in the dosage of sodium oleate to 800 g/t led to additional increase in P$_2$O$_5$ recovery by three percentage points while P$_2$O$_5$ grade remained similar (compare SP-7 and SP-8). Therefore, 800 g/t sodium oleate was appropriate in the flotation

of skarn phosphate. 800 g/t sodium oleate and 2 kg/t sodium silicate obviously resulted in a higher quartz/silicate entrainment and a poor phosphate concentrate. However, a bulk cleaner flotation following phosphate rougher flotation lowered the quartz/silicate recovery to the phosphate concentrate from about 25% to 13% while increasing the bulk phosphate concentrate grade by two percentage points and lowering the P_2O_5 recovery by about six percentage points. A bulk cleaner phosphate flotation was necessary, and it was therefore used in the subsequent tests.

In conclusion, 5 kg/t sodium carbonate, 2 kg/t sodium silicate, and 800 g/t sodium oleate are suitable reagent dosages for the direct rougher flotation of the Mactung skarn phosphate rock sample at a grind size of 86% passing 53 μm, and a bulk phosphate cleaner flotation is necessary to lower the quartz/silicates deportment into the phosphate concentrate.

3.3.3. Carbonate Reverse Flotation

During the reverse flotation of carbonate, combined sulfuric and phosphoric acids were used as phosphate depressants. The flotation conditions are listed in Table **??**, and the results are shown in Table **??**.

Table 6. Reagent dosages used in the reverse flotation of carbonate from the bulk skarn phosphate flotation concentrate.

Test #	Sulfuric Acid, kg/t	Phosphoric Acid, kg/t
SP-7	10	3
SP-8	12	7
SP-9	10	7
SP-10	10	9
SP-11	8	7

Table 7. The results of carbonate reverse flotation from bulk skarn phosphate flotation concentrate.

Test #	Products	Weight		Assay (XRF), (%)					Distribution (%)				
		(g)	(%)	P_2O_5	CaO	MgO	SiO_2	SO_3	P_2O_5	CaO	MgO	SiO_2	SO_3
SP-7	P Conc	145.0	29.34	24.32	46.66	1.26	7.22	0.00	57.55	44.06	21.68	6.68	0.00
	Ca Conc	64.5	13.05	18.63	53.50	1.31	3.16	0.00	19.61	22.47	10.02	1.30	0.00
	P+Ca Conc2	209.4	42.39	22.57	48.77	1.27	5.97	0.00	77.15	66.53	31.70	7.97	0.00
SP-8	P Conc	167.5	33.81	25.35	45.28	1.01	10.80	0.44	66.47	48.07	21.83	11.72	6.84
	Ca Conc	58.9	11.88	16.32	61.27	0.74	3.16	0.00	15.04	22.86	5.59	1.20	0.00
	P+Ca Conc2	226.3	45.70	23.01	49.44	0.94	8.81	0.33	81.51	70.94	27.43	12.93	6.84
SP-9	P Conc	154.7	31.30	27.34	44.84	0.85	7.12	0.27	65.89	43.49	19.92	7.34	4.53
	Ca Conc	65.8	13.32	13.47	63.36	0.64	3.16	0.00	13.82	26.15	6.42	1.38	0.00
	P+Ca Conc2	220.5	44.61	23.20	50.37	0.79	5.94	0.19	79.71	69.64	26.35	8.72	4.53
SP-10	P Conc	167.8	34.03	25.06	45.59	1.42	7.24	0.21	69.02	51.01	25.69	8.07	3.54
	Ca Conc	49.4	10.02	11.36	51.78	1.57	3.16	0.05	9.21	17.07	8.34	1.04	0.25
	P+Ca Conc2	217.2	44.05	21.95	47.00	1.45	6.31	0.17	78.24	68.08	34.03	9.11	3.79
SP-11	P Conc	159.0	31.97	26.85	45.46	1.70	9.22	0.00	65.63	45.27	30.23	9.33	0.00
	Ca Conc	65.9	13.25	15.94	62.46	0.71	3.16	0.00	16.15	25.78	5.28	1.32	0.00
	P+Ca Conc2	225.0	45.22	23.65	50.44	1.41	7.44	0.00	81.78	71.05	35.51	10.65	0.00

"P Conc" refers to the phosphate concentrate from the sink product of the reverse carbonate flotation stage; "Ca Conc" refers to the carbonate concentrate or phosphate tailings from the floated product of the reverse carbonate flotation stage; "P+Ca Conc2" refers to the feed ore for the carbonate reverse flotation.

By maintaining a constant sulfuric acid dosage of 10 kg/t, the increased dosage of phosphoric acid from 3 kg/t to 7 kg/t led to a significant improvement in the separation efficiency of phosphate from the carbonate gangue minerals (compare SP-7 and SP-9). The P_2O_5 grade and recovery were increased by three and eight percentage points, respectively. However, further increase in the dosage of phosphoric acid to 9 kg/t led to a slight increase

in P_2O_5 recovery of phosphate concentrate by about two percentage points while its grade was decreased by 1 percentage point (compare SP-9 and SP-10). Therefore, 7 kg/t was an optimum dosage of phosphoric acid.

At constant 7 kg/t phosphoric acid dosage, the decreased dosage of sulfuric acid from 12 kg/t to 10 kg/t resulted in two percentage points increase in P_2O_5 grade of phosphate concentrate but a slight decrease of about 0.5 percentage points in the P_2O_5 recovery (compare SP-8 and SP-9). Lowering the sulfuric acid dosage further to 8 kg/t slightly lowered the phosphate/carbonate separation efficiency. Therefore, 10 kg/t sulfuric acid is the optimal dosage to depress the phosphate while floating off the carbonate minerals. Due to carbonate dissolution, a relatively high consumption of both phosphoric acid and sulfuric acid were required to achieve a suitable acidic environment for an effective separation of phosphate minerals from the carbonate gangues.

Test SP-9 was carried out using optimized reagent dosages determined in the preliminary direct phosphate rougher flotation and reverse carbonate flotation stages and it produced the best flotation performance. A detailed flowsheet of the SP-9 test beneficiation is shown in Figure **??**. The products of the test were further validated by Bureau Veritas Commodities Canada Ltd., and the results and metallurgical mass balances are summarized in Table **??**.

Finally, a phosphate concentrate assaying 28.68 wt% P_2O_5, 12.06 wt% SiO_2, 46.89% CaO and 0.72 wt% MgO, at a P_2O_5 recovery of 70.9%, was produced after one phosphate rougher flotation, one bulk cleaner flotation and one stage of carbonate reverse flotation, at a grind size of 86% passing 53 μm. The reagent scheme of the entire flotation process was: 10 g/t PAX and 40 g/t MIBC for reverse sulfide flotation from the ore feed; 5 kg/t Na_2CO_3, 2 kg/t water glass and 800 g/t sodium oleate for direct phosphate rougher flotation from the sulfide flotation tail; 10 kg/t H_2SO_4 and 7 kg/t H_3PO_4 for carbonate reverse flotation from the phosphate concentrate.
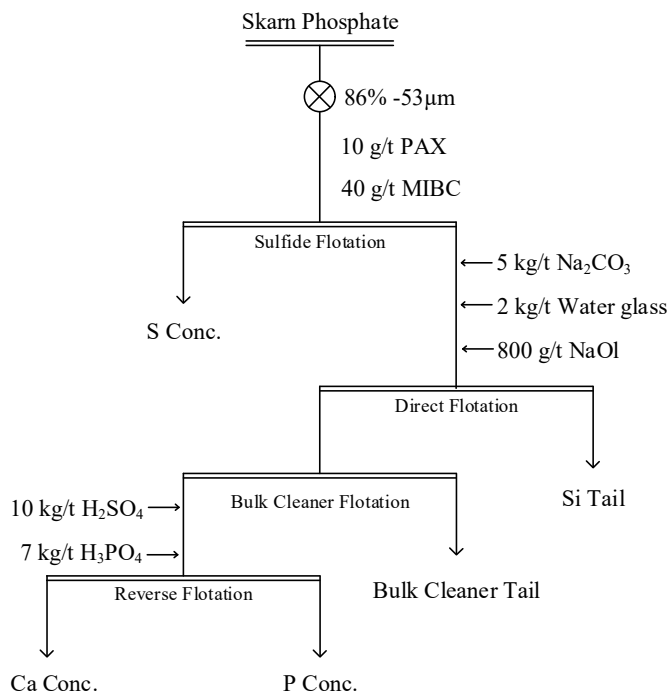
Figure 6. A detailed flowsheet of SP-9 beneficiation test.

Table 8. Results of batch flotation test SP-9 on skarn phosphate.

Products	Weight		Assay, (BV; %)					Distribution (%)				
	(g)	**(%)**	**P_2O_5**	**CaO**	**MgO**	**SiO_2**	**SO_3**	**P_2O_5**	**CaO**	**MgO**	**SiO_2**	**SO_3**
P Conc.	154.7	31.30	28.68	46.89	0.72	12.06	0.63	70.90	45.58	13.29	11.24	n/a
Ca Conc. 1	65.8	13.32	11.09	52.57	0.16	1.85	0.48	11.67	21.74	1.26	0.73	n/a
Ca+P Conc. 2	220.5	44.61	23.43	48.59	0.55	9.01	0.59	82.57	67.33	14.54	11.98	n/a
Bulk Tail	43.2	8.74	8.38	26.16	2.49	43.37	0.80	5.78	7.10	12.83	11.29	n/a
Ca+P Conc. 1	263.7	53.35	20.96	44.91	0.87	14.64	0.62	88.35	74.43	27.37	23.27	n/a
Si Tail1	210.9	42.67	2.27	16.23	2.76	58.40	2.17	7.65	21.51	69.44	74.24	n/a
S Tail	474.6	96.03	12.66	32.17	1.71	34.09	1.31	96.00	95.94	96.81	97.51	n/a
S Conc.	19.6	3.97	12.73	32.92	1.36	21.07	>10	4.00	4.06	3.19	2.49	n/a
Feed	494.3	100.00	12.66	32.20	1.70	33.57	n/a	100.00	100.00	100.00	100.00	n/a

4. Conclusions and Recommendations

A skarn phosphate rock sample from the Mactung tungsten deposit characterized by cryptocrystalline apatite (collophane) containing carbonate, sulfides, quartz and other silicates gangue minerals and assaying 12.65% P_2O_5, 1.75% MgO, 31.71% CaO and 35.46% SiO_2 was upgraded into a phosphate concentrate assaying 28.68% P_2O_5, 12.06% SiO_2, 0.72% MgO and 46.98% CaO, at a P_2O_5 recovery of 70.9%. The ore is hard with a Bond Work Index of 19.04 kWh/t.

Instead of allowing the phosphate in the mine waste and tailings, the phosphate resources can be recovered by a flowsheet comprising both direct and reverse flotation, which is a standard industry method for processing phosphate ores with a high carbonate content. The extraction would not only promote the local economy, but also protect the aquatic ecosystem from any phosphorous leakage that may otherwise cause algae bloom and eutrophication of lakes.

Although the final concentrate does not meet the fertilizer requirement of >30% P_2O_5 and CaO/P_2O_5 < 1.6, it is possible that further optimization of reagent dosages and grind or re-grind sizes in a flowsheet involving both direct and reverse flotations could produce an acceptable concentrate.

In addition, the phosphate rock may contain recoverable trace metals including rare earth elements that could further improve the economics of processing the phosphate. However, these were not evaluated in this study and we recommend an evaluation of their content in future studies.

The current reagent dosages were very high (several kilograms per ton), which would have negative impact on the profitability of the project. It is, therefore, recommended that further research should be carried out including reagents optimization, use of non-polar oil and new collectors and/or other phosphate depressants, as well as grinding or re-grinding sizes.

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