FLOTATION OF CHROMITE

This thesis is presented by M. T. Salman in part fulfillment of the requirements for the Degree of Master of Engineering.

McGill University, Montreal

April 1944

The investigations described in this paper were carried out by the writer under the direction of Mr. M. D. O'Shaughnessy, Lecturer in Mining Engineering in the Department of Mining and metallurgy at McGill University.

ACKNOWLEDGEMENTS

The writer wishes to express his indebtedness to Mr. M. D. O'Shaughnessy under whose general direction the research was conducted. His keen interest, constant co-operation and guidance were sincerely appreciated.

Special acknowledgement is given to Professor O. N. Brown, Associate Professor of Mining Engineering who rendered valuable assistance in all phases of the work and especially in chemical analysis experiments.

The careful and helpful assistance given by Mr. Hugh McBride, laboratory assistant, is also gratefully acknowledged.

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PART ONE

INTRODUCTION

Flotation process is undoubtedly the most important development in the recovery of metals from ores that has taken place during the present century. No other method of ore treatment has ever effected such great changes in metallurgical practice in so short a time.

The industrial importance,can be emphasized best by considering the non-ferrous metal mining industry. At the period under question practically every mining district has witnessed almost complete exhaustion of high grade oxidized ores near the surface and often of the high grade sulphides in the so-called zones of secondary enrichment, leaving only the low grade primary sulphides usually more or less complex in the lower levels. Hence the companies were thus confronted with increased mining costs, lower grade ores and high treatment charges. In many cases it became economically impossible to mine and ship the sulphides at all. The only alternative was to introduce some method of mechanical concentration. Eventually these methods all lead to flotation practice.

To-day concentration of sulphide ores of copper, sulphide-lead-zinc ores, copper-zinc, copper-lead, copper-nickel ores, precious and rare metals is successfully accomplished in many plants.

In many respects these methods of concentration are simple to carry out and most universally successful. To-day the tonnage of sulphide copper ore treated annually by flotation is about 70,000,000 tons of which approximately two thirds is in United States.

Due to early investigations and successful operations flotation has been closely allied with the sulphide minerals and flotation literature has dealt primarily with the removal of sulphides from non-metallic gangue and the separation of one sulphide from another.

Now the application of the process to the separation of non-sulphide minerals is coming to the fore , and from the standpoint of a number of commercial minerals involved the flotation of non-sulphides offers the larger field.

Among the non-metallics, the minerals sulphur, graphite and talc are classed as "natural floaters". They respond to almost any type of flotation and their benefication by flotation had been attempted years ago. Flotation of sulphur is now common practice and graphite was concentrated during the last war, Talc has also been floated on a commercial scale.

Second to the natural floaters come the "easy floaters", Cassiterite, Fluorite, Barite, Mica and Paper Pulp from white water of paper mills.

Among the outstanding achievements in the benefication of non-metallics has been the froth flotation of phosphate rock, cement rock, limestone, fluorite and potash salts.

Coming to flotation of chromite, no commercial scale of operation has been attempted as far as the writer knows. Yet chromite is imported to the North American continent from the South Pacific, Southern Rhodesia, Czechoslovakia and Turkey.

In Canada during peace time the cost of importing chromium is much less than the cost of treating the comparatively low grade chromite deposits. For this reason the utilization of Canada's domestic chromite ores has been feasible only under the abnormal economic conditions set up by international war. Under such conditions with import supplies cut off there then remains no alternative, but to work the existing ore bodies. During these periods chromite concentrate containing as little as 30% Cr_2O_3 was accepted by the consumers while the manufacturers of chromium alloys in peace time generally specify that the chromite must contain at least 45% Cr_2O_3 and the ratio of chromic oxide to iron oxide should exceed 3:1 and furthermore they require lump ore.

The writer is of the opinion that these requirements and penalties are some of the reasons why froth flotation is not applied to chromite concentration.

As for the previous work done along this line, not much has been published except a few articles which are not very specific in their statements. Among these O. C. Ralston mentions the use of fatty acids and their soaps in concentration. Steve Dembicki has tried to float the same ore which the author has worked and got some interesting results, but was not able to bring out effective concentration.

PROBLEM

Chromium is one of the less common metals. Recognition of its valuable properties led to its uses in our ever increasing variety of industries. This growing demand has, in turn led to the search for new deposits of chromite, the only commercial ore of the metal and to a revival of interest in known deposits of low grade ore.

Virtually the whole of Canada's production of chromite has come from deposits in the Eastern Townships of the Province of Quebec. Of the chromite deposits in the Eastern Townships one of the most promising is that of the Sterrett Mine. The property was opened up in 1916 and after producing till 1919 was closed due to high milling costs.

With Canada's entry into the present war the property was reopened in August, 1940. Since then much work has been done on the property.

Chromite ores are concentrated by gravity concentration using tables, jigs and accessory equipment. The crushing and grinding operations carried out preliminary to jigging and tabling operations inevitably produce a good deal of very finely divided mineral. Much of this fine mineral is too fine to be recovered in jigging and tabling and as a result is lost in the concentration process. This loss amounts to 4.5 - 6.5% Cr_2O_3. One percent recovery of Cr_2O_3 from this tailing is about a hundred dollars gain per day.

The tests described in this thesis were made to study the possibilities of concentration by flotation as applied to Sterrett Mine chromite or in general concentration of similar low grade chromite deposits. An attempt was also made to increase the efficiency of chromite concentration by eliminating some of the loss of the finer sizes.

Before the flotation tests the problem of Iron Determination in Chromite was presented to the writer by Mister M. D. O'Shaughnessy.

While he worked in Sterrett Mine he noticed the difficulties encountered in the chemical assay laboratory. The samples were run in triplicate The using Vanadium Corporation method for iron determination. The results were erratic and the percent of errors were not within the limits of permissable errors allowed in ordinary quantitative analysis methods. In some cases two of the results in a triple run agreed with one another but this was not consistent. Furthermore the results of samples purposely prepared and sent to different chemical analysts did not check with one another.

PREPARATION FOR CHEMICAL ANALYSIS

A shipment of 53.5 pounds of table concentrate chromite was received from Chromite Limited. It was dried in a steam oven which gave a gross weight of 51.56 pounds. Prior to actual riffling this material was thoroughly mixed. In a systematic series of stages ten 2000 gram samples were then carefully riffled out on Brunton riffles. These ten samples were weighed to within one gram, placed in clean air tight tins, properly labelled and set aside. The residue left behind was partly used for screen analysis.

One 2000 gram sample was cut into four 500 grams and one of these was pulverized to give -100 mesh product. Then a representative sample of 100 grams was taken from this for chemical analysis.

VANADIUM CORPORATION METHOD

Before starting any experimenting the author thought it would be beneficial to formulate all the reactions taking place when using the method.

One gram, -100 mesh ore is weighed and thoroughly mixed in a porcelain crucible with 10 grams sodium peroxide by means of a glass rod. Cover the mixture with one gram of sodium peroxide. Place crucible on a triangle and slowly heat until mixture melts. With the aid of crucible tongs slowly fuse with a rotating motion, avoiding at all times too great a temperature to cause mixture to spatter. The reaction between chromite mineral and sodium peroxide is:-

$$2\ Fe\ Cr_2O_4 + 7\ Na_2O_2 \longrightarrow Fe_2O_3 + 4\ Na_2CrO_4 + 3\ Na_2O$$

Hence chromium is brought into solution as $CrO_4^{=}$ ion.

Allow the crucible to cool, then place in a 600 ml. beaker containing 400 ml. of water plus one gram of ammonium carbonate. Cover and bring to boil. Boil five minutes. Remove crucible. Reactions are:-

$Na_2O_2 + 2\ H_2O\ (cold) \longrightarrow 2NaOH + H_2O_2 \uparrow$

$Na_2O + H_2O \longrightarrow 2NaOH$

$2\ Na_2O_2 + 2H_2O\ (warm) \longrightarrow 4NaOH + O_2 \uparrow$

When boiled - $2H_2O_2 + heat \longrightarrow 2H_2O + O_2 \uparrow$

As seen from above reactions, the solution is strong in NaOH, which might attack the filter paper. Hence ammonium carbonate is added to reduce this effect.

$$2\ NaOH + (NH_4)_2CO_3 \longrightarrow Na_2CO_3 + 2\ NH_4OH$$

In strong basic solution we obtain a reddish brown precipitate.

$Fe^{++} + 2OH^{-} \leftrightarrows Fe(OH)_2 \downarrow$

$Fe(OH)_2 + O_2 + 2H_2O \leftrightarrows 4Fe(OH)_3 \downarrow$

Allow precipitate to settle. Filter through a paper of close texture.

Wash with hot water containing a small piece of sodium hydroxide. Dissolve precipitate into original beaker with hot 1-4 Hcl acid. Hence $Fe(OH)_3$ is converted into $FeCl_3$.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

which goes into solution as Fe^{+++} ion. Wash thoroughly, add 15 ml. saturated solution of bromium water and boil for ten minutes. Render ammoniacal with ammonium hydroxide. Boil and filter. Wash with hot water containing very little ammonium hydroxide. Dissolve the original beaker with hot 1-5 sulphuric acid. The reaction being:

$$Fe(OH)_3 + 3H^{+} \quad Fe^{+++} + 3H_2O$$

Wash thoroughly keeping volume approximately 150 ml., add 4 ml. concentrated hydrochloric acid. Bring solution to boil and reduce with stannous chloride.

$$Fe^{+++} + Sn^{++} \longrightarrow Sn^{++++} + 2Fe^{++}$$

Cool, add cold water and bring volume to 400 ml. Add 25 ml. saturated solution of mercuric chloride. Stir well, add 25 ml. titrating mixture, again stir. Titrate to first permanent pink colour of clear solution with standard $KMnO_4$.

COMMENTS ON THE METHOD FOR BETTER RESULTS

It is clearly seen from the above reasoning that the addition of hydrochloric acid is a very important step in titration. All the $Fe(OH)_3$ is brought into solution. The method requires 4 ml. HCl acid. This amount must be sufficient to bring all the iron into solution as ferric chloride. An excess of hydrochloric acid might cause some trouble when titrating with $KMnO_4$ if the solution is not cold and very dilute. Hence when using the above method to get consistent results we must use exactly the same amount of hydrochloric acid.

A second point is that of reduction with stannous chloride. First an excess of stannous chloride must be used to ensure complete reduction of iron and the excess must be removed or it will react with $KMnO_4$. Mercuric chloride is added, which oxidizes all the remaining Sn^{++} and is itself reduced to mercurous chloride, which precipitates

$$Sn^{++} + 2Hg^{++} + 2Cl^{-} \longrightarrow Sn^{++++} + Hg_2Cl_2\downarrow$$

The solubility of Hg_2Cl_2 is so small that it does not react appreciably with $KMnO_4$. Only the smallest possible excess of $SnCl_2$ is used since if much Sn^{++} ion remains in solution it may reduce some of $HgCl_2$ to free metallic mercury which would react with $KMnO_4$. If the precipitate is grayish, due to finely divided mercury, instead of pure white Hg_2Cl_2 the analysis must be discarded. The $SnCl_2$ is added to the hot solution in which the reduction proceeds rapidly but the solution is cooled before the $HgCl_2$ is added because as soon as the excess of Sn^{++} is eliminated the oxygen of the air can re-oxidize Fe^{++} to Fe^{+++} and would do so appreciably in a short time if the solution were hot. The solution must be allowed to stand for a few minutes after adding the $HgCl_2$ to give the precipitate of Hg_2Cl_2 time to separate out, but the titration must be made without further delay because the atmospheric oxidation of the iron proceeds slowly even in cold solution.

IRON DETERMINATION EXPERIMENTS

Using the described method a few tests were run. In these few tests some difficulty was encountered with the end point. Then with extra care good end points were obtained but the results were not in close agreement. Hence it was evident that there was some cause for this deviation. The writer thought that this was due to excess of HCl acid. To study this effect some experiments were run with pure iron wire. The results of the tests are shown in Table I.

TABLE I

Test No.	1	2	3
Iron Used (gms.)	0.128	0.127	0.128
Iron Determined (gms.)	0.130	0.130	0.129
% Error	1.56(+)	2.36(+)	0.8(+)

As seen from the above results, there is a positive error in all the tests.

Similar experiments were run with varying amounts of HCl. The results showed, as HCl was increased up to a point the errors were negative, after a certain amount the errors were positive. Hence it became evident that there was a certain critical HCl value. Negative errors are very easily explained, because all the iron was not altered to ferric-chloride. But it was hard to explain the positive errors, because in dilute cold solutions HCl acid is not supposed to react with $KMnO_4$. In our case if we assume that it does the explanation is that some HCl which is left over is reacting with $KMnO_4$ and hence giving higher results. To ascertain this point analysis were run with varied amounts of HCl.

TABLE II

Test No.	1	2	3	4	5	6
HCl used	2.00	3.00	4.00	5.00	6.00	7.00
Iron used	0.1221	0.1235	0.1260	0.1245	0.1261	0.1255
Iron Determined	0.1213	0.1238	.1265	0.1294	0.1318	0.1344
% Error	0.65(-)	0.24(+)	0.39(+)	3.9(+)	4.5(+)	7.9(+)

From the results in Table II it is clearly seen that there is a critical HCl and above that value the errors are all positive increasing with HCl. To avoid this we must have very dilute solution of HCl and titration must be done when solution is very cold.

MODIFIED METHOD

Due to the above difficulties with the Vanadium Corporation method the writer thought of a certain modification. The approach to the problem was as follows. With pure iron wire iron determinations were carried out using sulphuric acid method. The procedure being:- weigh 0.128 gms. of iron wire (or ore). Place it into 120 cc. beaker add 2 cc. water and 10 cc. HCl, digest and add 5 cc. HNO_3. Boil till brown fumes cease. Cool, add 5 - 10 cc. 1:1 H_2SO_4 and fume strongly. Add water and boil to dissolve the sulphates. Filter, washing five or six times with hot water. To each beaker add a strip of aluminum (pure) and boil to reduce the iron. When solution is colorless remove, cool, wash off the aluminum strips and dilute to 250 cc. for titrating with standard $KMnO_4$. Five tests were run with the above method. The results are shown in Table III.

TABLE III

Test No.	1	2	3	4	5
Iron Wire gm.	0.1266	0.1246	0.1232	0.1243	0.1255
Iron Determined	0.1265	0.1245	0.1231	0.1242	0.1252
% Error	0.06(-)	0.04(-)	0.06(-)	0.06(-)	0.18(-)

From the above results it is clearly seen that, the agreement is very close. The negative error in all cases may be explained by the small oxidation of ferrous iron to ferric, while titrating or the iron wire may contain slight impurities.

Now we are in a position to introduce the modification. Vanadium Corporation Method should be followed up to the point where it is required to add 4 ml. HCl (concentrated). Instead cool the beaker and fume strongly. Cool and add 10 cc. H_2O and boil to dissolve the sulphates. To each beaker add a strip of pure aluminum and boil to reduce the iron. When the solution is colorless, cool, wash off the aluminum strips, filter and dilute to 250 cc. and titrate with $KMnO_4$.

With this modification 5 tests were run with Chromite Ore, the results are:- (Table IV).

TABLE IV

Test No.	1	2	3	4	5
$KMnO_4$	26.57	26.57	26.56	26.57	26.57
%(Fe_2O_3)	13.17	13.17	13.16	13.17	13.17

CONCLUSIONS

(1) Vanadium Corporation Method will give results with the right amount of HCl acid.

(2) Reduction with $SnCl_2$ should be done very carefully.

(3) Dilution and the temperature of the solution before titration should be such that excess HCl acid wouldn't react with $KMnO_4$ and hence give higher iron value.

(4) Modified method is simpler and does not require as much care in reduction stage.

(5) When using Aluminum, Zinc, Cadmium or Lead the assayer should make sure that they are pure. If they are not, a correction may be made by means of a blank titration.

PART II-A

FLOTATION TESTS WITH TABLE CONCENTRATE

FATTY ACID AND SOAP FLOTATION

Early investigators in flotation of non-metallics recommend fatty acids and their soaps for most of the oxides. Since chromite is an oxide it was decided to investigate the possibility of commercial fatty acid and soap flotation on Sterrett Mine Chromite.

For quick quantitative results the writer designed a small pneumatic cell about 200 - 300 grams capacity. The air was pumped through a blanket and the pressure could be adjusted so that it gave the right amount of froth. Reagents were added in a systematic way and frothing, collecting properties of the pulp were examined. Using oleic acid ($C_{17}H_{33}COOH$), sodium Oleate ($C_{17}H_{33}COONa$), pine oil and sodium carbonate in varying amounts on table concentrate chromite, various preliminary experiments were made. The writer observed the following results.

When using oleic acid in a pulp made alkaline with sodium carbonate, oleic acid showed both collecting and frothing power, but the bubbles obtained were stable and armoured with the mineral.

When sodium oleate was used instead of oleic acid, the reaction was entirely similar.

At this stage of the work it was found quite instructive to try to find out whether it is the acid or the soap which is the real collector and what is the nature of adsorption or chemical reaction taking place.

When chromite concentrate is agitated in a solution of sodium oleate (one pound per ton), the soapy froth first present disappears in one or two minutes and at the same time chromite becomes coagulated and forms heavily mineralized froth. At the same time pH of the solution increases.

Results of the test are as follows:-

500 cc. water containing 0.025 gms. sodium oleate, pH of the solution is 7.15, when 50 gms. of chromite is added the pH is 7.60. The same sample of chromite added to water increased the pH to 7.20.

Hence the increase in pH observed when chromite was added to the sodium oleate solution cannot be ascribed to any alkaline constituent of the chromite used. The conclusion cannot be avoided that the fatty acid only is abstracted from solution and that the alkaline base remains in solution.

Now let us try to explain the mechanism of frothing and collection.

We have oleic acid which is a polar compound with an unsymmetrical form. When a drop of oleic acid is placed on water it spreads over the surface to give a film of one molecule deep. Since the carboxyl group of the acid dissolves in water, the molecules of acid orient themselves, with carboxyl group in the water and hydrocarbon tails pack in side by side vertically above the carboxyl layer. (Figure I) The reason of insolubility in water is that the affinity of long hydro-carbon chain for water is less than their affinity for each other. If such a long hydro-carbon chain happens to get inside the water they effect a separation of water molecules, but since the attraction of water molecules for each other is higher than for the hydro-carbon chain, when the water molecules get together by kinetic motion they tend to stay together and thus force out the hydro-carbon chains.

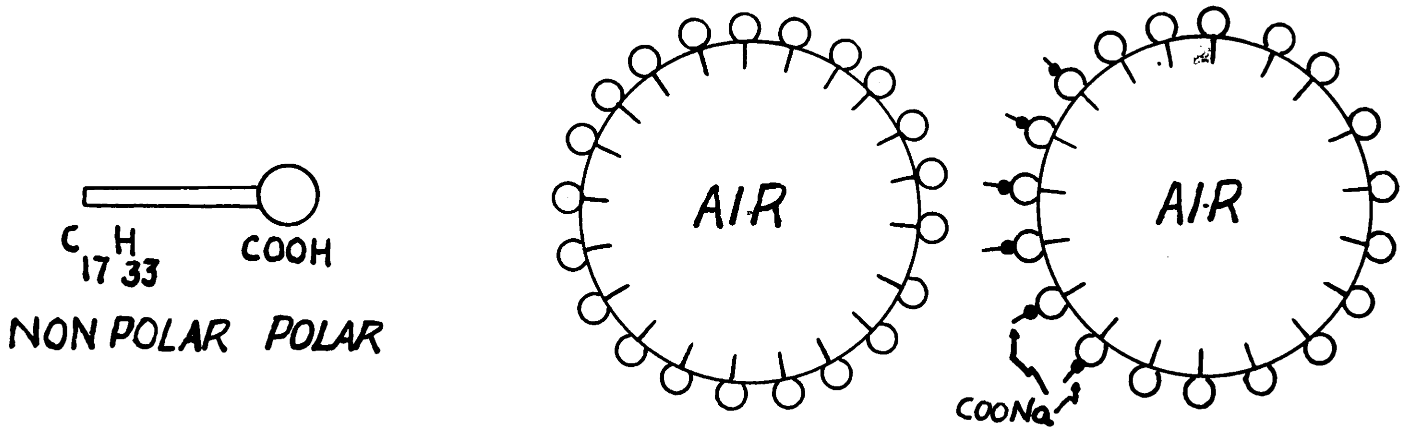


FIGURE 1

This film, however, is not viscous enough to give a stable froth, solid particles concentrate at the interface and give a stable foam of armoured bubbles. Hence better results are obtained by the use of oil containing a soluble constituent which acts as a foam former in place of a straight insoluble oil.

Furthermore according to Bancroft's theory of emulsions we have for sodium oleate the following theory.

Polar emulsifying agents such as the soaps are probably oriented in the surface film with hydro-carbon end of the molecules towards the oil phase and carboxyl group with its metallic radical towards the water phase. Hence as a result of the above hypothesis we can say that the collection-frothing mechanism is as shown (Figure I).

Now let us try to explain the actual collection. From qualitative tests it was evident that oleic acid is the primary collector. This was also justified by the fact that it was oleic acid which decreased in the process. As for sodium oleate in solution, from McBain's investigations we have the following:-

Sodium Oleate at certain concentrations dissociates to give $C_{17}H_{33}COO^-$ anions which agglomerate to form highly hydrous colloidal particles with the formula $(C_{17}H_{33}COO^-)_n\ mH_2O$. In other concentration ranges, neutral colloidal soap particles $(C_{17}H_{33}COO\ Na)_x mH_2O$ may exist and still other there may be no colloidal particles but only $C_{17}H_{33}COO\ Na \rightleftarrows Na^+ + C_{17}H_{33}COO^-$. Hence the nature of a soap solution varies with its concentration and its temperature.

Since we are dealing with small concentration (1 - 5 lbs. per ton of ore) most probably sodium oleate is mostly in ionic form and this is the form which brings about the collection, if any.

Considering the pulp, soap, a salt of a strong base and a weak acid is somewhat hydrolized.

$$\begin{array}{l} C_{17}H_{33}COO\ Na \leftrightarrows Na^+ + C_{17}H_{33}COO^- \\ \qquad\qquad\qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad\qquad\qquad\quad H^- + HO^- \leftrightarrows H_2O \\ \qquad\qquad\qquad\qquad\qquad\quad \updownarrow \\ \qquad\qquad\qquad\qquad\quad C_{17}H_{33}COOH \end{array}$$

An equilibrium exists in solution between the fatty acid and sodium hydroxide. If the mineral adsorbs the fatty acid, the equilibrium will be disturbed and hydrolysis will proceed and liberate new quantities of sodium hydroxide. Hence the solution will become more alkaline.

The second explanation is based on the chemical theory of Taggart, which assumes that the soap reacts chemically with the mineral forming an insoluble metallic soap.

In either of the above explanations when the mineral is floated with oleic acid, the base in solution and the mineral complete against each other for the reaction with the fatty acid. In this case chromite abstracts some of the oleic acid, which is not available any more for making soap and frothing, sodium carbonate reacts with some oleic acid which is not available any more for collecting the mineral.

When the mineral is floated with soap the situation is entirely the same. In other words an increase in pH increases the frothing and decreases the collecting power of the fatty acid or soap.

Hence from the above results it is clearly seen that there is a certain critical pH which would give best collecting and best frothing properties. To find this value some qualitative experiments were done using 1.0 lbs. per ton sodium oleate, 1.0 lbs. per ton Oleic acid and sodium carbonate was added systematically as shown. The pH of the pulp was determined after every addition and the sample of the froth taken was mounted on plasticine for microscopic examination.

TABLE V

Critical pH determination for 1.0 $\frac{\text{lbs.}}{\text{ton}}$ Na-Oleate, 1.0 $\frac{\text{lbs.}}{\text{ton}}$ Oleic Acid

Na_2CO_3(lbs./ton)	PH	Frothing and collecting
0.0	7.20	↓
1	9.90	
2.0	10.22	
3.0	10.45	
4.0	10.55	
5.0	10.65	↓ Good froth & collection
6.0	10.75	Decrease of collecting power.
7.0	10.85	
8.0	10.90	
9.0	11.05	
11.0	11.15	↓

The results of the tests are shown in Table V.

PHYSICAL PROPERTIES OF THE ORE

Ore used was a part of the ore left over in the McGill Mining laboratories from S. Dembicki's experiments. Originally this was sent by Cyril L. Jerrom, Vice-President CHROMITE LIMITED and was shipped from the Sterrett Mine which is located about three and a half miles south-east of St. Cyr station on the Canadian National Railway.

CHEMICAL COMPOSITION

The ore consists of three or more metallic minerals and at least the same number of gangue minerals. The metallic minerals include chromite, magnetite and minute traces of pyrite. Among the gangue material there is serpentine and some carbonate mineral which is most probably calcite or dolomite. Of the metallic minerals chromite is the most abundant. Actual quantity of magnetite is very small. Serpentine predominates among the gangue minerals. Traversing this granular serpentine are occasional narrow veinlets of chrysolite.

A complete series of analysies were carried out by Mr. M. Archambault in the laboratories of Ecole Polytechnique, Montreal, who determined in each case the following constituents: SiO_2, Al_2O_3, Cr_2O_3, MgO, CaO, Fe_2O_3, and FeO. The results on carefully purified concentrates show that they contain 50.90% Cr_2O_3 and 13.50% FeO.

GRAIN SIZE DETERMINATION

Detailed microscopic tests were carried out on polished sections by S. Dembicki and he found that of all the chromite grains measured, 81.5% had a dimension between 0.377 millimeters and 2.262 millimeters. His conclusions were that by grinding the ore to 35 mesh product 89% of the chromite could be liberated. Assuming 35 mesh as the largest particles in the grind the average size would be 0.209 millimeters. (Calculation being based on recent work in crushing and grinding which states that the average particle size of flotation pulps is of the order of one twentieth the size of the coarsest particles).

To check the above result the problem was attacked from a different point of view.

A screen anlaysis was run on the table concentrate from the mill which contained about 49 - 50% Cr_2O_3 and the average size of this concentrate was determined.

(SCREEN ANALYSIS ON TABLE CONCENTRATE)

Size, Mesh	Average Size of Grade (cm.) (n)	Volume abundance percent (f)	$\frac{f}{n}$
20-28	0.0711	3	42.1
28-35	0.0503	17	348.1
35-48	0.0356	20	561.0
48-65	0.0251	16	638.0
65-100	0.0178	20	1121.0
100-150	0.0125	11	880.0
150-200	0.0089	8	898.0
200-270	0.0063	5	792.0
	$\therefore x = \frac{100}{\sum \frac{f}{n}} =$	0.190 mm.	$\sum \frac{f}{n} = 5280.2$

As seen from the calculation the two results are in close agreement.

PART II-B

FLOTATION TESTS WITH THE ORE

PREPARATION OF FEED

A bag of 45 pounds -0.192" ore was taken and in a systematic series of stages, eight 2000-gms. samples were carefully riffled out on Brunton riffles. These eight samples were weighed to within one gram, placed in clean, air tight tins, properly labelled and set aside for subsequent tests. One of these 2000 gram samples was again riffled and 8 samples of 250 gms. were prepared for the small flotation machine.

DETERMINATION OF PROPER GRIND

It is quite evident that for every ore there is a certain well defined size range for optimum recovery and another well defined size range for optimum selection. Hence it was decided to find out these ranges before attempting some actual flotation tests.

With respect to the fineness of grinding necessary for flotation first we have to consider the complete liberation of the mineral from the gangue. For the ore used this limit as found is about 35 mesh.

Assuming quiescent conditions and perfect unwettability the calculated maximum size at which flotation should be possible is 3.7 millimeters. However although particles of chromite 3.7

millimeters in diameter are floatable under quiescent conditions, it is naturally not to be expected that this should hold under the conditions of violent agitation prevailing in a flotation machine.

As to the minimum floatable size, since the supporting force of a particle at the surface of a liquid is proportional to the perimeter of the particle, whereas the principle force opposing it is proportional to the cube of the particle diameter, it is clear that, leaving other forces than gravity and surface tension, the finer the particle the easier it is to keep it supported at a gas-liquid interface. Yet investigations show that fine particles are not as readily floated as might be expected. A. M. Gaudin after a series of experiments concludes that the most probable hypothesis is the probability of fine particles adhering to air bubbles or having air precipitated on their surface is much smaller than the similar probability in the case of coarser particles. Hence fine particles should not float as completely as coarse particles and more time should be required to complete flotation.

To obtain the most suitable grind a series of rod mill tests were run on 300 gram and 2000 gram samples. Results examined under the microscope to save time. For 300 gram samples, 5 minutes and for 2000 gram samples 30 minutes grind was found to be most suitable. In both cases the coarsest particles of the grinds were +35 mesh (0.417 millimeters). Hence the average size of the particles in the pulp was approximately 400 mesh.

To see the size range and the percentage of each range a screen analysis was run on one of the 2000 gram samples. The sample was washed with water through a 200 mesh screen to remove the minus 200 mesh slime, then dried, weighed, and screened in the Bell screening machine. Results of the run are shown in the accompanying table.

TABLE VI

Mesh	Wt. of Screen (gms.)	Percent
+ 35	0.07	0.07
+ 48	0.06	0.06
+ 65	0.86	0.90
+ 100	5.81	6.17
+ 150	13.82	14.60
+ 200	22.46	23.80
- 200	9.53	10.66
- 200 (slimes)	41.79	43.74
TOTAL	94.40	100.00

From these results average size calculation of the grind was made with the assumption that average dimension of slime particles were 0.001 mm. It gave the average size of the grind as 400 mesh also.

TABLE VII

Mesh	Average Size of Grade (cm.) (n)	Volume abundance percent (f)	$\frac{f}{n}$
28-35	0.0503	0.07	1.4
35-48	0.0356	0.06	1.7
48-65	0.0251	0.90	3.6
65-100	0.0178	6.17	346.5
100-150	0.0125	14.60	1165.5
150-200	0.0089	23.80	2670.0
200-270	0.0063	10.66	1695.0
270-Av.Slime diam.	0.0027	43.74	16200.0
	Av. Size $(x) = \frac{100}{\Sigma \frac{f}{n}} = 0.04$ mm.		22083.7

AMENABILITY TESTS

To determine whether the flotation process was applicable various amenability tests were made. Different combinations of oleic acid, sodium oleate, and sodium carbonate and pine oil were tried in the pneumatic cell. No selectivity and no concentration of any kind was obtained. The author is of the opinion that this was due to the action of the slimes.

The ore as mentioned before contains two varieties of serpentine. One irregular granular type which results from the alteration of olivine and the other variety is the fibrous type which is most probably chrysotile. In addition we have some carbonate which is most probably dolomite. From the results of various grinding tests it was noticed that increasing grinding increased the amount of fibrous slime. In the flotation pulp the fibrous slimes get coagulated and all the particles are coated with carbonate slime. Since the specific gravity of the fibres is less than any other constituents this fibrous mat floats at the top. The gangue and chromite settle to the bottom. Reagents used to float are absorbed by this mat.

Furthermore there was flocculation in the pulp. It was believed that the flocs consisted mainly of the fibrous gangue minerals and that as the flocs were formed the finely divided chromite particles were entrapped in the mass.

Along these lines S. Dembicki tried various deflocculation tests using different reagents. The author's conclusion from the results obtained is that it is practically impossible to get any selectivity from the ground ore as it comes from the grinding circuit.

DESLIMING AND ITS EFFECTS

Various experiments were tried with 200 - 300 gram samples. Each taken and ground in the rod mill with 50% moisture using ordinary tap water. Then the rod mill product was taken out and deslimed by hand as completely as possible. The procedure employed was to put the contents in a tub with addition of four to five times the quantity of water and after stirring the contents by hand decant the slimes off carefully. This operation was repeated five or six times. Care was taken not to produce any concentration. Naturally this was practically impossible. As a result some of the fine chromite and gangue was carried away with the slime. This deslimed material was taken and put into the small pneumatic cell and flotation attempted.

The results of a sample with two minutes grind is shown in the table below.

TABLE VIII

Ore	Reagents Used	
Deslimed ore = 215.0 gms. Ground 2 min. with 50% moisture pH of the pulp = 8.1	First Float: 0.40 lbs./ton Na.Oleate 0.50 lbs./ton Oleic Acid 0.10 lbs./ton Pine Oil	Second Float: 1.0 lbs./ton Na.Oleate 1.0 lbs./ton Oleic Acid 0.2 lbs./ton Pine Oil

Product	Weight per cent	Cr_2O_3(%)	Recovery
Concentrate	15.82	49.0	28.7
Middling	26.50	38.3	
Tailing	57.68	15.5	
	100.00	27.0	

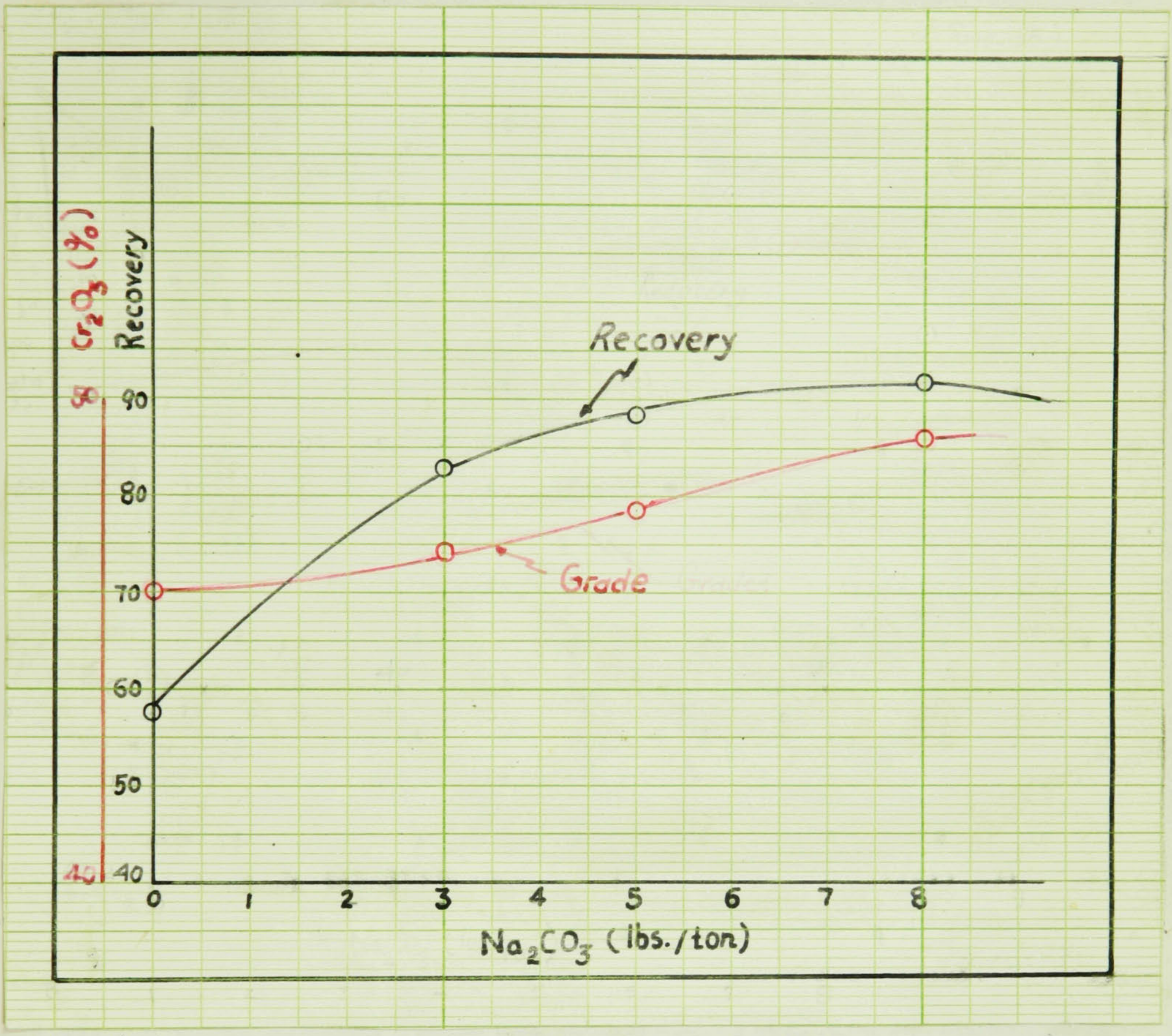
With this test chromite as coarse as +48 mesh was floated. Hence it is clearly seen that under these conditions it is possible to float chromite, but in the above test the recovery is low. Observations on the concentrate, middling and tailing showed that the grind was too coarse. As mentioned before five minutes grind is found to be most suitable.

MOST SUITABLE REAGENT COMBINATION

In preliminary tests with the table concentrate I showed that there was a critical pH for the best collecting and frothing properties when using fatty acids and their soaps for flotation. With the following experiments this effect was studied quantitatively. In this respect some experiments were tried with lime. The results obtained were not satisfactory and it was found out that lime had a slight depressing effect on chromite, hence decreased selectivity. Sodium carbonate gave the most satisfactory results. Keeping the amounts of oleic acid, sodium oleate and pine oil constant, the effect of increase in sodium carbonate on recovery and grade was studied. The results of the five tests are shown in the table. As seen from the results an increase in Na_2CO_3, improved the grade of the concentrate and also increased the recovery.

TABLE IX

Test No.	1		2		3		4	
Reagents Used	2.0 lbs/ton Na.Oleate 1.1 lbs/ton Oleic Acid 0.1 lbs/ton Pine Oil		Same		Same		2.0 lbs./ton Na. Oleate 0.1 lbs./ton Pine Oil	
Na_2CO_3(lbs/ton)	0.0		3.0		5.0		8.0	
	Wt. (%)	Cr_2O_3(%)	Wt.(%)	Cr_2O_3(%)	Wt.(%)	Cr_2O_3(%)	Wt.(%)	Cr_2O_3(%)
Concentrate	38.5	46.0	56.0	46.8	52.9	47.7	60.5	49.2
Tailing	61.5	21.4	44.0	8.2	47.1	7.2	39.5	6.6
Feed	100.0	31.0	100.0	31.6	100.0	29.6	100.0	32.3
Recovery	57.1		83.0		88.3		92.0	



Looking at test No.5 with 8 lbs. per ton Na_2CO_3 no oleic acid is required and a concentrate which contains 49.2% Cr_2O_3 is obtained with a recovery of 92.0 (%), pH of the pulp was 9.5. Further increase in Na_2CO_3 decreased ~~with~~ the recovery and the grade. This fact was justified by examining the samples on plasticine under the microscope and comparing them with standard analyzed samples which the author had prepared for quick comparison.

TESTS WITH STANDARD 500 GM. GLASS BOWL FAGERGREN AND 2000 GM. DENVER SUB-A FLOTATION CELLS

After the promising results as obtained with the small laboratory pneumatic flotation cell the author thought of standardizing these results. For this purpose 500 gm. Fagergren and 2000 gm. Denver Sub-A flotation cells were used.

The first few 500 gm. samples were prepared with the usual procedure described in the first section of this thesis. Then the ground samples were deslimed with a laboratory size Wilfley Table. The pulp as it came out from the rod mill was introduced in a cone feeder and it was fed to the table with a $\frac{3''}{16}$ orifice and constant overflow. At the start the table was horizontal, then as the slimes in the pulp decreased it was tilted slightly. The deslimed ore was then filtered and placed in Fagergren flotation cell. Using ~~exactly~~ identical reagent combination flotation was attempted.

The results were entirely different to what was expected. A thick grayish froth was obtained. There was no selectivity and no concentration. The chromite and gangue particles which were in the froth looked as though they were just entrapped due to agitation of the cell. Addition of extra reagents did not alter the conditions at all.

Similar tests were tried with Denver Sub-A flotation cell using 2000 gm. samples. Identical thick skummy froth was obtained with no selectivity.

First the author thought that this effect could be eliminated by using dispersing agents. Using Na_2SiO_3, gelatinous Na_2SiO_3 (i.e. water glass), $Na_2S.9H_2O$, concentrated NH_4OH and NaOH similar results were obtained. Among the above reagents gelatinous Na_2SiO_3 was found to be most effective, but it was also a strong depressant for chromite, equally well as the gangue. With the time available various combinations were tried without any success.

Since all other conditions governing flotation of the ore are identical, except the types of machines used, an explanation of this unexpected phenomenon evidently is related to the bubble production, bubble attachment and agitation of the pulp into two types. To justify this assumption a test was run using the same amount of reagents with a small impeller agitator. A thick skummy froth, similar to the one obtained in agitation cell was obtained.

The froth examined under a microscope consisted of small bubbles completely coated with slimes.

Investigation of the bubble formation process by observation of the operation in the glass sided machines showed that:-

(1) Bubbles are much larger in pneumatic machines.

(2) They are more numerous.

(3) They rise through the pulp more rapidly.

With these facts as a basis the following explanation is proposed.

In agitation machines the bubbles produced are much smaller in diameter, furthermore the shearing action of the fast rotating impeller breaks these bubbles still further. As a result we obtain a large quantity of small bubbles with an enormous surface area. Hence the slimes have a better chance of coating the surfaces. Once these small bubbles are coated with slimes they are held together by fibrous slimes, hence a thick skummy froth is obtained. Naturally once the surface of the bubbles is coated with slimes the physical and chemical conditions of solid-air attachment is changed,hence the affinity of air to non-polar surfaces is decreased, hence no collectivity.

PART III

FLOTATION TESTS WITH TAILINGS OF STERRETT MINE MILL

INTRODUCTION

Normal peacetime specifications for metallurgical chrome ore call for a grade of 48% Cr_2O_3 and a chromium-iron ratio of 3 to 1; lump ore is preferred to concentrate. At the present, lump ore or concentrates with a chromium-iron ratio of 6 to 2 are used for making ferro-chromium and material with still lower ratios and as little as 35% Cr_2O_3 is accepted for mixing with high grade imported ore.

Requirements vary greatly in the manufacture of refractory material but it is important that the silica content be low and the percentage of the iron not too high as both reduce the fusion point. Prices vary according to the composition and the grade of the ore and are usually determined by contract between the buyer and seller.

Present Canadian prices for high grade ore or concentrate containing 48% Cr_2O_3 and having a chromium-iron ratio of 3 to 1 are $45.75 per long ton, U.S. funds f.o.b. Niagara Falls. For poorer grades or qualities within limits, there is a deduction of 90¢ per ton for each 1% and of $1.25 for each 0.1 in the chromium-iron ratio. Low grade crude ores carrying 35 - 40% Cr_2O_3 have recently brought prices ranging from $20 to $28 per long ton on the cars, but it is difficult to sell small lots.

Hence it is evident that if the flotation process could be applied to the tailing which contains about 6 - 7% Cr_2O_3 and a fair concentration is obtained the amount of money saved would be considerable. Assuming that a success in the laboratory was obtained; the application of the method to industry would naturally call for a profitable balance between the expenses for such a treatment which may include, desliming equipment, probably extra grinding equipment and all instulations for a flotation circuit and the profit obtained after selling the product.

My problem, however, essentially is to investigate the application of flotation to such a tailing. If successful results are obtained,the economical balance,if there is any could be obtained by men who are authorities on mill design.

PREPARATION OF FEED

A shipment of a sack of tailing, total weight 83.0 pounds was received on February 1, 1941. The sample was shipped from the Sterrett Mine. After being completely dried, broken and screened through $\frac{1}{16}$" screen, four samples were prepared, each being 2263.0 grams. From one of these a gram sample was taken for screen analysis. The sample was washed with water through a 200 mesh screen to remove the minus 200 mesh slimes, then dried and weighed and screened in the Bell screening machine. To see the variation of Cr_2O_3 with screen size chemical analysis were run on accumlative weights as shown in the table.

SCREEN ANALYSIS OF TAILING

Mesh	Av. Size (mm.)	Actual Percentage	Cumulative Percentage	Cr_2O_3(%)
+14	0.711	0.21	21.76	4.90
+20		3.20		
+28		18.35		
+35	0.251	13.21	31.66	5.66
+48		8.17		
+65		10.28		
+100	0.089	7.71	16.52	4.44
+150		4.25		
+200		4.56		
-200	0.063	1.48	30.06	8.23
-200(slimes)		28.58		
		100.00	100.00	6.05

As seen from the table most of the chromite is in -200 mesh and -200 mesh slimes. Hence we can avoid grinding the tailing by using all the -65 mesh material as flotation feed. This material contains more than fifty percent of chromite in the tailing. Chromite in +65 mesh material will be discarded because, firstly it is a ~~very~~ small loss, secondly if we wanted to recover it by flotation we would have to regrind the tailing which is quite an expensive proposition.

FLOTATION TESTS

First two of the prepared samples were taken and the -65 mesh material recovered. Since this material contained a large percentage of fibrous slimes it was found necessary to deslime it. Starting the test with 2263.0 gms., the amount ready for flotation test was 180 gms. from one sample and 191.0 gms. from the other giving a total of 371.0 gms. A flotation test was carried on this sample using 5 lbs./ton Na_2CO_3, 2 lbs./ton Sodium Oleate, 1.1 lbs./ton Oleic Acid and 0.1 lbs./ton Pine Oil.

With the other two samples similar procedure was followed only the amount of Na_2CO_3 changed to 10 lbs./ton instead of using 5.0 lbs./ton. The results of the two tests are shown in the following table.

FLOTATION TESTS WITH TAILING

Test No.	Product	Weight(%)	Cr_2O_3(%)	Recovery
I	Concentrate	25.3	16.6	64.5
	Tailing	74.7	3.10	
	Feed	100.0	6.51	
II	Concentrate	26.5	17.5	67.1
	Tailing	73.5	3.1	
	Feed	100.0	6.92	

As seen from the table the chromite content of the feed in two tests are different (i.e. 6.51 and 6.92% Cr_2O_3). Naturally this is due to the desliming of the -65 mesh material. Looking at the grades of concentrates we can easily see that they are nowhere near the requirements of the market. As seen, the recovery and grade increased in the second test, but still the grade is way below the specifications.

Hence the above results are only of academic interest. They show that there is a definite concentration and the amount of Na_2CO_3 has a noticeable effect in increasing the recovery and also in improving the grade.

With the closing of the university term it was found necessary to conclude the tests at this stage.

However, I am convinced that the recovery of chromite from tailing can be accomplished by flotation. This may be done either by using the same reagents in a different combination or by using altogether different set of reagents. As to the nature of reagents to be used I am not in a position to predict. However as a suggestion I will recommend stronger acids of the Fatty acid group.

SUMMARY AND CONCLUSION

In the preceding pages the writer has endeavoured to describe and explain certain tests conducted in an effort to solve the following problems:-

(1) Iron determination of Chromite ores.

(2) Application of flotation in concentration of Chromite ore.

(3) Possible increase of efficiency of concentration by ordinary gravity methods, by application of flotation to the tails. Hence the loss of finely divided chromite.

Tests were made on Chromite ore, table concentrate and tailing which were shipped from the Sterrett mine, one of the most promising chromite deposits in the Eastern Townships of Quebec.

In iron determination experiments first the Vanadium Corporation method was used. The method first brings the Fe Cr_2O_4 to Na_2CrO_4 which is ionized and is taken away with the filtrate. The precipitate ferric-hydroxide. Then this is dissolved by HCl acid which brings the iron in to ferric-ion state. Then ferric iron is reduced to ferrous-ion by stannous chloride and the solution titrated with standard $KMnO_4$ for iron content. As discussed in detail the above method is simple but it has certain draw-backs.

From the results obtained it is important that the minimum amount of HCl acid be used, just sufficient to transform iron from sulphate to chloride. If excess HCl acid is used and the solution is not very dilute with respect to HCl acid and not cold, this excess will react with $KMnO_4$ to give high iron values for the ore.

To get rid of this and other difficulties, such as reduction with stannous-chloride (which is not very difficult but requires extra care) a new method was proposed. The results obtained were very satisfactory and I am of the opinion that it is simpler.

Flotation tests were first tried with table concentrate and collecting properties of Oleic acid and Sodium-oleate studied. With sodium-carbonate it was found that collecting and frothing properties were modified so that at a critical pH best conditions could be obtained.

The results of the flotation tests with the ore led to the conclusion that it was practically impossible to obtain any selectivity unless the ore were deslimed completely. In this respect dispersing agents were found to be entirely useless.

For quick results a small pneumatic flotation cell was designed, hence it was possible to treat 200-300 grams of ground ore at a time. From a series of experiments using proper reagents a good concentrate was obtained which contained 49.2% Cr_2O_3 and recovery of the operation was 92%. The reagents used were 8 lbs./ton sodium carbonate, 2.0 lbs./ton sodium oleate and 0.1 lbs./ton pine oil.

pH determinations showed that an increase in pH increased the frothing and decreased the collecting power of the collector. Hence a critical pH was present for best collecting power. This value was found by keeping the amount of sodium-oleate, oleic acid and pine oil constant but by changing the amount of sodium carbonate.

Up to this point all the experiments were done in the small pneumatic cell. Then the problem was to deslime the ore with a standard table and use a standard cell for flotation.

Using the same amounts of reagents under identical conditions no concentrate was obtained. Various reagent combinations were tried without any success. This was thought to be due to violent agitation in the cell, with the combined effect of slimes. There was no standard pneumatic cell available in the laboratory at the time therefore similar experiments could not be performed with it.

The time available for tailing experiments was limited but the results obtained are encouraging. From the result of the tests it became quite evident that there is a definite concentration and selectivity. Starting with 6.92% Cr_2O_3 material a concentrate which contained 17.5% Cr_2O_3 was obtained with a recovery of 67.1%. Although this result is encouraging it is nowhere near the requirements of the market. However this can be improved by a second cleaning process.

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