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THE METALLURGICAL TREATMENT OF CANADIAN
PYRRHOTITE ORES BY LEACHING AND ELECTROLYTIC
DEPOSITION, AND OF CANADIAN PYRITE ORES BY
ROASTING, LEACHING, AND ELECTROLYTIC
DEPOSITION; WITH THE PRODUCTION OF ELECTRO-
LYTIC IRON, AND THE RECOVERY OF BY-PRODUCTS
SUCH AS SULPHUR, COPPER, ETC.

by
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INTRODUCTORY

An investigation to determine the suitability of a leaching and electrolytic method of treatment for pyrrhotite and pyrite ores in connection with their possible utilization in the manufacture of electrolytic iron, was started in November 1922.

The preparation of electrolytic iron has been a subject of scientific study and research for about 80 years, but it is only during the last 15 or 20 years with the realization of its unusual physical and chemical properties, that metallurgists and chemists have turned their attention toward establishing for it a practical industrial process. Processes are in operation at the present time in France, Germany and America, producing an iron of 99.9% to 99.97% purity, from pig iron or scrap used as anodes in an electrolyte of ferrous salts, with and without additional reagents, on steel cathodes of either sheet or rotating mandrel form

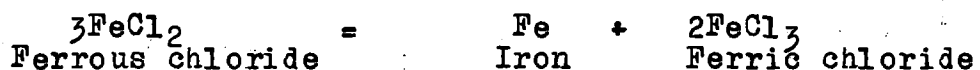
Electrolytic iron has unusual mechanical and electrical properties which open up many special fields of usefulness, and it is in

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demand in the making of special steel or alloys, boiler tubes, electrical machinery, wire, and articles to be nickel plated or galvanized, etc.

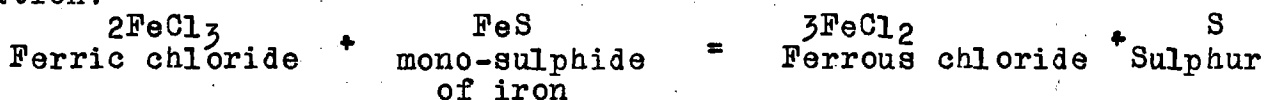
THE EUSTIS PROCESS

F. A. Eustis of Boston and C. P. Perin of New York have patented what is known as the Eustis process, with the idea of utilizing iron ores directly. It differs from preceding processes in that an insoluble anode is used, and a diaphragm separates the anolyte and catholyte. In the cell iron is deposited on the cathode while oxidation of the ferrous chloride takes place at the anode. The ferric chloride thus formed in the anode compartment is led over the raw pyrrhotite ore (pyrite requires special treatment) effecting the solution of the iron and simultaneously reducing the ferric chloride to the ferrous state. Sulphur is deposited in the gangue and is recovered as brimstone. The chemistry of the cell reaction may be shown as



The production of ferric chloride is directly proportional to the amount of iron deposited

The reaction of the ferric chloride and ore may be shown by the equation:



From these equations it will be seen that exactly the amount of iron removed by electrolysis is restored to the solution, and the process becomes cyclical.

In an ore containing copper the copper dissolved must be removed, probably by precipitation on scrap iron, and can be readily recovered as a by-product. It is claimed for the process that 90% of the iron may be recovered as pure electrolytic iron and 90% or more of the sulphur as brimstone. The current density may be varied over a wide range, 20-100 amp. per sq. ft. and the voltage from 1-4.5 volts

THE ESTELLE PROCESS

The Estelle process which in some respects is similar to the above, has been patented by Axel Estelle.

In this process the suitably prepared ore is heated with a weak non-oxidizing acid, preferably hydrochloric, at a temperature of 40-80 C. The results of the reaction is the formation of ferrous chloride and sulphuretted hydrogen.. The ferrous chloride goes to the electrolytic cell where a portion of the iron is deposited and twice this amount of iron is converted to ferric chloride. The sulphuretted hydrogen set free in the acid-ore reaction is collected in absorptions towers and used for the reduction of the ferric chloride from the cell, hydrochloric acid being set free with separation of sulphur. The hydrochloric acid previously combined with the non-electrolytically deposited is in this manner again liberated and made available for leaching fresh ore.

It is claimed for this process that other "Sulphur containing metals" present remain with the gangue, and can be readily recovered in this concentrated condition, also that the sulphur is eliminated in a separate apparatus in a fairly pure condition.

LABORATORY INVESTIGATIONS.

The laboratories of the Ore Dressing and Metallurgical Division plan to investigate the possibilities of each of these processes, and is at the present time conducting tests on the Eustis process. The work done so far has been of a very preliminary nature and only on a small laboratory scale. The following brief description of tests are submitted to demonstrate the possibilities of the leaching process as applied to pyrrhotite and pyrite ores.

GENERAL PROCEDURE FOLLOWED.

An enamel pail of 5-6 litres capacity, fitted with a wooden cover, was used as a leaching tank. Agitation was accomplished by a rotating wooden agitator. Steam was used for maintaining the temperature necessary for leaching. The ferric chloride used was ordinary grade containing about 20% iron.

It was found that steam passing into a cold or slightly warm solution of ferric chloride hydrolyzed the ferric chloride to an appreciable extent, and the iron so hydrolyzed would be lost as oxychloride of iron in the gangue. By passing the steam into a hot solution, or a slightly acid solution the hydrolytic dissociation was greatly reduced. Heating directly with steam causes a dilution of solution due to condensation of the steam, and the increase in volume has been as much as 18% in two hours running on a 3 litre test. This problem of heating the solution will probably be more readily overcome in a continuous circuit process, as the electrolyte will be hot, due to the action of the current. It may also be observed here that the reaction between the ore and the ferric chloride is exothermic to the extent of 20,400 calories or 700 B.T.U. per pound of iron dissolved.

For laboratory tests a steam jacket method of heating was found most satisfactory; there was a loss of course in volume due to evaporation amounting to 5-15%, but the hydrolytically dissociated iron was greatly reduced.

According to theory, in the leaching process 2 parts of iron as ferric chloride should dissolve 1 part iron from the ore, resulting in the formation of 3 parts iron as ferrous chloride

TEST NO. 181

A shipment of pyrrhotite ore received in November from the Smith property, west side of Lake Memphremagog, Que., was used in the following tests. This ore on analysis was found to be about 80% pyrrhotite, 25% chalcopyrite, 2.5% lime (CaO). The iron content averaged 49.5%, and the copper 0.85%

Leaching test #1

Quantities used:

3.0 litres ferric chloride at 70 grams per litre	= 210
	grms Fe.
235 grams ore (-200 mesh at 49.5% Fe	= 116.5
	gms Fe.

This amount of ore would be about 11% in excess of theoretical requirement.

The ore and solution were put in pail and heated by passing steam

into the solution, agitating at the same time, until temperature had reached 95 C. which temperature was maintained for 2 hours. The solution was allowed to cool and was then filtered, increase of volume being 18.3%. Theoretically the 210 grams of Fe. in the ferric chloride should react with 105 grams of Fe in the ore to form 315 grams of ferrous iron.

Analysis of solution showed that 252 grams of ferrous iron had been formed which is 80% of theoretical amount or in other words 84 grams of iron were leached out of the ore. Had the time of leaching been extended, it is probable that a much higher recovery would have been made.

Leaching test no. 3 This test was run to obtain data concerning the rate of reaction when using a high excess of ore, and to obtain some information on counter-current extraction and also on the behaviour of copper in the ore.

Quantities used:

3.5 litres ferric chloride at 66 grams per litre	=	231	grams	Fe.
335 grams ore (-200 mesh) at 49.6% Fe	=	165.8	"	"
and at 0.85% Cu	=	2.85	"	Cu

This amount of ore would be about 45% in excess of theoretical

The solution was heated to 75 C. by steam jacket method, ore added, and the temperature increased to and held at 95 C.

Solution sampled after 30 minutes leaching contained	85	g/l	ferrous	Fe
" " " 60 " " "	92.5	"	"	"
" " " 90 " " "	105	"	"	"
" " " 120 " " "	106	"	"	"

Reaction considered complete, no ferric iron present. Time 2 hours.

Volume of solution after cooling and filtering = 3.10 litres

Analysis showed total ferrous iron = 328.6 grams

Theoretically 231 grams of Fe in the ferric chloride would react with 115.5 grams Fe in the ore to give 346.5 grams of ferrous iron, so that 328.6 grams ferrous iron found is equal to 95% of the theoretical, or 109.5 grams of iron were leached from the ore.

The residue weighed 206 grams and contained 30.6% Fe or 63 grams. Theoretically Fe in residue should be the amount of iron in quantity of ore used, minus amount of iron dissolved in leaching, which would be 165.8 - 109.5 = 56.3 grams. It was found, however, that ferric

chloride hydrolyzed and oxychloride of iron precipitated, hence this excess of 6.7 grams in the residue is probably due to (1) iron hydrolytically dissociated, and (2) iron precipitated by lime present in ore.

The copper in residue amounted to 1.17% or 2.41 grams, therefore, the amount of copper leached was 15.3%

Leaching of residue: 180 grams of this residue containing 55 grams Fe. and 2.106 grams Cu. were treated with 3.4 litres solution containing 45 grams/litres ferrous Fe = 153 gr. Fe
" 32 " " ferric Fe = 108.8 "

Conditions of leaching similar to first part of test. After 2½ hours leaching analysis of solution showed a content of 73 grams/litre ferrous Fe. and 17 grams/litre ferric Fe.

Volume of solution after cooling and filtering = 3.125 litres
Total ferrous iron is 228.3 grams and ferric iron 53 grams.

The result shows that 25 grams of Fe in the residue has been leached out
The copper content of the residue was 0.65%, weight of residue 150 grms.

Combining the results of these two tests it is found that:

Total extraction of iron = 83.4%
" " copper = 61.6%

Summing up it may be said that when a large excess of ore is used the reaction is very rapid and a completely reduced ferrous chloride solution is produced. In practice this reaction would take place in the primary agitators. In the treatment of the residue from this first action, which would take place in the secondary agitators, the reaction would be much slower, due possibly to the liberated sulphur forming a protective coating over the ore particles.

In the above test a higher extraction would probably have resulted had the period of extraction in the secondary action been extended.

As a result of the several tests made, it has been found that fine grinding of the pyrrhotite is essential and that the leaching process should be conducted at a temperature around 90-95 C. Best results have been obtained by grinding to minus 200 mesh (.0029 inch opening) and leaching at 95 C.

PYRITE TREATMENT

Pyrite (FeS_2) is not readily attacked by ferric chloride, and requires preliminary treatment. This treatment consists of converting the pyrite into a variety of pyrrhotite, soluble in ferric chloride, by roasting in a neutral or reducing atmosphere at a temperature of 700-750 C. Under these conditions one atom of sulphur is driven off and with suitable apparatus can be recovered as a by-product

TEST NO. 182

A shipment of pyrite received November 1922 from the Eustis mine, Eustis, Quebec, was used in the following test:

Chemical analysis of ore: Iron 41.2%; copper 1.55%; Lead 0.75%; sulphur 46.7%. This would be about 85% pyrite and 4.5% chalcopyrite

Screen analysis showed:

	<u>Sample weight</u>	<u>Per-cent</u>	<u>Per-cent accumulative</u>
Held on 35 mesh (.0164" opening)	14	7	7
" 48 " (.0116" ")	28	14	21
" 65 " (.0082" ")	40	20	41
" 100 " (.0059" ")	48	24	65
" 150 " (.0041" ")	28	14	79
" 200 " (.0029" ")	28	14	93
Passing 200 " (.0029" ")	14	7	100
	<hr/> 200	<hr/> 100	

Pyrite Roasting: Three samples of 150 grams each were placed in a piece of wrought iron pipe 8" x 1½", closed at one end with a cap. These were placed in a small electric muffle furnace and roasted at a temperature ranging from 700 to 750 C.. An examination after 45 minutes roasting showed incomplete roasting, particles of pyrite being observed. Analysis gave 39% iron in ferrous condition. A further 45 minutes roast was made, and resulting product showed 48.2% ferrous iron and a magnetic test showed 91% of the roasted material to be magnetic. The samples all checked very closely, the third sample being roasted for two hours gave results similar to the 1½ hour roast. Analysis of roasted material was:

Iron (total)	50.00%
Copper	1.90%
Lead	0.92%
Total sulphur	33.30%

Of the iron, 97.2% was present in the ferrous condition. A small amount of SO_3 was present as originally in the raw ore. From further analytical data obtained, the composition of the roast would be somewhat as follows:

FeS₉, 79.35% Cu₂S 2.38% FeS₂ 2.67%

Leaching: A quantity of the roasted material ground to pass a 200 mesh screen (.0029" opening) was leached with a solution of ferrous and ferric chlorides under conditions of temperature and agitation similar to those pertaining in the leaching of pyrrhotite.

The reduction of the ferric chloride and leaching did not occur quite as rapidly as with natural pyrrhotite, 210 grams ore requiring 7 hours leaching with a solution containing 308 grams Fe as ferrous chloride and 209 grams Fe as ferric chloride; excess of ore considering copper and lead, being about 6.5%. However, results showed extraction of 85% of the iron, 42% of the copper, and practically 100% of the lead.

GENERAL CONCLUSIONS.

The results obtained in these tests, though being of a very preliminary nature show that this method of treatment for pyrrhotite and pyrite is very promising. So far as the iron is concerned it would appear that recoveries of over 80% could readily be made.

Concerning copper, the results are not so encouraging, the copper going partly into solution and partly with the gangue. This problem as well as the separation and recovery of other metallic sulphides occurring in these ores will be gone into in the investigation contemplated.

The laboratory at present is not equipped with electrolytic apparatus, and so it has not been possible to study the electro-deposition phase of the process. However, plans are being prepared with this end in view, and it is hoped that a continuous circuit suited to the proper study of this process will be installed in the near future, when the process may be investigated under conditions approaching more closely those that would obtain in actual practice.