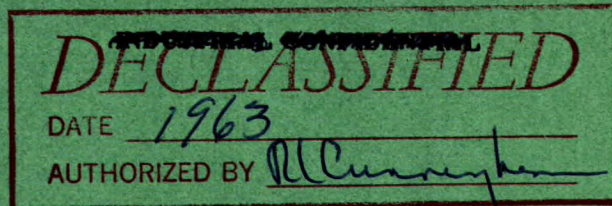


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MINES BRANCH INVESTIGATION REPORT IR 61-71

THE CALCINATION OF ALGOMA SIDERITE ORE

by

NORMAN F. H. BRIGHT & RICHARD H. LAKE

MINERAL SCIENCES DIVISION

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Norman F.H. Bright* and Richard H. Lake**

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SUMMARY OF RESULTS

The Algoma siderite ore has been shown to consist of a complex mixture of mineral carbonates of which siderite (FeCO_3) is the most abundant species. Other carbonates present include iron-bearing rhodocrosite, magnesite, calcite, dolomite and ankerite.

The techniques used to derive this information included differential thermal analysis, thermogravimetric analysis, X-ray diffraction, semi-quantitative emission spectroscopy and wet chemical analysis.

The products of calcination depend on the temperature and atmosphere used during the heating. The predominant phase is a complex spinel solid solution which may contain magnetite, maghemite (or γ -hematite) and various ferrites.

In a magnetising roast, some iron may be lost in a non-magnetic form by the formation of the compound $\text{CaCO}_3 \cdot \text{Fe}_2\text{O}_3$, or by reversion of γ -hematite to α -hematite.

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INTRODUCTION

In September, 1960, representatives of The Algoma Steel Corporation, Limited, visited the Mines Branch, Ottawa, to discuss the calcination of the ore, which is one of the main raw materials in their iron and steel operations. The ore, which comes predominantly from the Michipicoten area of Ontario, was stated to be mainly sideritic in nature. The points on which technological assistance were requested were:-

- a) What reactions occur when the siderite ore is calcined, and, in particular, what oxide(s) of iron are produced?
- b) How are these reactions affected by the atmosphere in which the calcination is conducted?
- c) What are the optimum conditions of atmosphere and temperature for the production of a calcined product having the highest practicable iron content?

Some samples of the Algoma ore were supplied for examination at the time of these discussions.

On November 4th, 1960, Mr. Carl M. Beck, General Manager of the Algoma Ore Properties Division of The Algoma Steel Corporation, Limited, visited the Mines Branch and held discussions with a group of members of the Mines Branch staff,

some from the Mineral Sciences Division, some from the Extraction Metallurgy Division, and some from the Mineral Processing Division, who were interested, respectively, in the chemistry of the calcination, the practical pyrometallurgy of the ore, and in the mineral dressing aspects of the problem. Mr. Beck was shown the various experimental facilities, including differential thermal analysis and thermogravimetric analysis, that were available for the study of the calcination process in the Physical Chemistry Section of the Mineral Sciences Division. As a result of this visit, two letters were received from Mr. Beck on November 8th, 1960, which are given as Appendices I and II to this report (see pages 30 to 31). These letters were again concerned with the nature of the iron oxide(s) formed on calcination. A reply to this letter was sent on November 16th, 1960 (see Appendix III).

As a result of these discussions, and in order to simplify the problem to some extent by removal from the ore of as much arsenic and sulphur as could conveniently be extracted, a sample of flotation concentrate from the Helen Mine of the Michipicoten field was sent to the Mines Branch on November 24th for examination.

Since that time, some calcined samples have been submitted by the Extraction Metallurgy Division to the Mineral Sciences Division for examination.

This report deals with the results obtained in the Mineral Sciences Division on the examination of these various samples. Any work performed by other Divisions of the Mines Branch will be reported separately.

EXPERIMENTAL

A. Techniques Employed

Several techniques were employed in this investigation, namely differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction examination (XRD), and, to a lesser extent, chemical and spectrographic analysis, and microscopy. Brief details concerning these various techniques, which are all standardised procedures, are given below.

(a) Differential Thermal Analysis

The technique of DTA is well-known and need not be described in detail here. In the current tests, the heating rate was 12 deg C per minute. The samples were heated in either a palladium metal or in a sintered alumina sample holder, using α -alumina as the standard reference material. Pt to Pt:13% Rh thermocouples were used to measure the sample and differential temperatures. Experiments were made in air and in flushing CO₂ atmospheres from room temperature up to 1100-1200°C. The use of the CO₂ atmosphere enabled certain oxidation reactions to be suppressed, thereby simplifying some of the results obtained; it also served to obtain better definition and resolution of the various endothermic carbonate-decomposition peaks which were encountered in the course of this work.

(b) Thermogravimetric Analysis

The thermogravimetric analyses were conducted using a Stanton recording thermobalance. The heating rate was approximately 385 deg C per hour. Again, tests were made both in air and in carbon dioxide atmospheres, and were conducted up to temperatures of approximately 1300-1400°C. The sample weights were also determined directly on an analytical balance, both before and after the experiments, as a check on the thermobalance readings.

(c) X-ray Diffraction

The samples, as received, and also after various thermal treatments, were submitted to the standard procedures of X-ray diffraction examination. Solid rollings of the crushed materials were examined using filtered CoK or FeK radiations in 57.3 mm Debye-Scherrer powder cameras. The resulting patterns were measured and interpreted, as far as possible, by comparison with the data published in the X-ray Powder Data File issued by the American Society for Testing Materials, or with standard patterns in the possession of the Physical Chemistry Section.

(d) Chemical and Spectrographic Examination

In order to provide additional information concerning the reactions occurring on the calcination of the siderite, certain samples were submitted to the Chemical and Spectrographic Laboratories of the Mines Branch for appropriate analyses.

(e) Microscopy

Polished sections of pieces of calcined ore were examined in reflected light in order to provide information on the uniformity or otherwise of the calcination, and on the number and relative abundance of the various phases present.

B. Results Obtained

(a) DTA and TGA Results

It will be convenient to discuss the DTA and TGA experiments concurrently and to correlate the results obtained by the two techniques.

The head sample of the ore, as received, when examined by DTA and TGA in air, gave the indications shown in Table 1 (page 6). The total weight loss was 28.4%, based on the weight of starting material.

It is obvious that the calcination process is complex and that several reactions, spread over a considerable range of temperatures, are occurring. In order to elucidate these phenomena, experiments were conducted in a carbon dioxide atmosphere. Several DTA runs were made; the individual runs varied somewhat in their indications, but the figures quoted in Table 2 (page 7) represent the mean of the several sets of observations obtained. Only one TGA run in a carbon dioxide atmosphere was made.

TABLE 1

DTA and TGA Results on Algoma Siderite Head Sample
(Heated in air)

Temperature Range (deg C)	DTA Observations	Temperature Range (deg C)	TGA Observations
Room temperature to 455°C	Very small <u>endo</u> -thermic peak at 336°C. Moderate, double <u>exo</u> thermic peak at 419° and 440°C.	Room temperature to 455°C	Very little significant weight change. Slight increase (0.1%) in range 375-415°C.
455°C to 640°C	Very large <u>endo</u> -thermic peak at 601°C, with shoulder at 560°C.	455°C to 640°C	Large, unresolved weight loss of 4.5% up to 525°C and additional 15.0% up to 640°C.
640°C to 955°C	Very large <u>exo</u> -thermic peak extending over whole range with smaller, <u>endo</u> -thermic peaks superimposed at 685°C and 786°C.	640°C to 955°C	Additional continuous weight loss of 3.4%, taking place in several unresolved stages.
955°C to 1090°C (end of run).	Small <u>endo</u> thermic peak at 985°C, followed by larger, incomplete <u>endo</u> -thermic peak extending beyond end of run.	955°C to 1350°C (end of run)	Additional weight loss of 5.5%, partly resolved into at least two stages, one between 955°C and 1040°C, and the other larger one between 1040°C and 1300°C.

TABLE 2

DTA and TGA Results on Algoma Siderite Head Sample
(Heated in Carbon Dioxide)

Temperature Range (deg C)	DTA Observations	Temperature Range (deg C)	TGA Observations
Room temperature to 415°C	Very small <u>endo</u> -thermic peak at 331°C.	Room temperature to 415°C	Very little significant change in weight; slight increase (0.1%) in range 300-415°C.
415°C to 555°C	Moderate <u>exothermic</u> peak in some cases at 435°C. Moderate <u>endothermic</u> peak at 547°C.	415°C to 555°C	Loss in weight at gradually increasing rate to 2.8%. (Net loss then 2.7%).
555°C to 635°C	Very large <u>endo</u> -thermic peak at 600°C.	555°C to 635°C	Large additional rapid weight loss of 22.5%.
635°C to 730°C	Moderate <u>endothermic</u> peak at 680°C with shoulder on high-temperature side of peak.	635°C to 730°C	Additional weight loss of 0.9%.
730°C to 880°C	Small <u>exothermic</u> peak at temperatures in the range 740-760°C. Moderate <u>endothermic</u> peak at 777°C with shoulder at 840°C.	730°C to 880°C	No observable corresponding weight change. Additional weight loss of 1.5%.
880°C to 1020°C	Additional moderate <u>endothermic</u> peaks at 936°C and 1010°C.	880°C to 1020°C	Additional unresolved weight loss of 1.1%.
1020°C to 1150°C	No clear-cut indication. Runs stopped at this temperature.	1020°C to 1180°C	Slight gain in weight in this range of 0.4%.

The DTA indications above 800°C in the CO₂ atmosphere were not very reproducible, partly due to excessive shrinkage of the specimens, leading to poor contact with the thermocouples, and partly due to imperfection of the protection offered by the CO₂ atmosphere. However, the figures quoted in Table 2 are taken from the most reasonable DTA traces.

These various DTA peaks imply the presence of a quite complex assemblage of minerals, and the interpretation of the results will be discussed later in the report.

Numerous other DTA and TGA examinations were made on a selection of products derived from the Algoma ore. These are as follows:-

1. Non-magnetic Fraction of the Flotation Concentrate from the Helen Mine Ore.
2. Black material selected from the Head Sample of Algoma Siderite.
3. Yellowish material selected from the Head Sample of Algoma Siderite.
4. Sulphitic Siderite selected from the Head Sample of Algoma Siderite.
5. Calcined Product from Algoma Ore.
6. Jeffrey Tailing from Algoma Ore.
7. Davis Tube Tailing from Algoma Ore.

The results obtained with these various materials will not be discussed until the evidence obtained from the other techniques has been presented and interpreted.

Very little information, additional to that available from the study of the head sample, was gleaned from these fractions (see page 26).

(b) X-ray Diffraction Results

X-ray diffraction examinations were conducted on the products of various calcination treatments of the ore by the Pyrometallurgy Section of the Extraction Metallurgy Division of the Mines Branch. The exact conditions under which these calcinations and subsequent fractionation of the products were conducted were not specified when the samples were submitted, but it is of interest to note the X-ray findings on the general nature of the calcination products. Certain chemical analyses of the products were provided. The details are given in Table 3.

Table 4 presents the X-ray findings on another series of products resulting from experiments styled "T-Grid Experiments" by the Pyrometallurgy Section.

TABLE 3

X-Ray Examination of Product of Kiln Experiment
No. P60-19-81

X-ray Lab. No.	X-ray Film No.	Analytical Lab. No.	Sample	Chemical Analysis					%Iron Recovery	X-ray Findings
				% As	%Fe ²⁺	%Fe ³⁺	% Total Fe	% SiO ₂		
XL1498	X9505	4719	Calcine, Dec. 14, 1960. Head Sample	0.125	14.2	31.7	45.9	-	-	Major:-Spinel Large minor:- Quartz Trace:- Hematite Pyrrhotite
	X9506	4718	Davis Tube Tailings	-	-	-	17.6	-	8.5	Major:-Quartz Large minor:- Pyrrhotite Small minor:- Hematite
	X9507	4745	Jeffrey Tailings	-	-	-	18.5	-	9.4	Major:-Quartz Large minor:- Pyrrhotite Small minor:- Hematite Trace:-Spinel
	X9508	4744	Jeffrey Middlings	0.187	-	-	41.3	13.70	3.8	Major:-Spinel, Quartz Small minor:- Hematite Pyrrhotite

Note: In Tables 3 and 4, the X-ray diffraction data were obtained by Mr. J.F. Rowland and Mr. E.J. Murray of the Physical Chemistry Section, Mineral Sciences Division. The chemical analyses were performed in the laboratories of the Control Analysis Section of the Extraction Metallurgy Division, under the direction of Mr. J.C. Ingles.

TABLE 4

X-Ray Findings on Products of "T-Grid Experiments"

X-ray Lab. No.	X-ray Film No.	Analytical Lab. No.	Pyrometallurgy Experiment No.	Analyses of Davis Tube Concentrates					Analyses of Davis Tube Tailings		X-ray Findings		
				% As	% S	% SiO ₂	% Fe	% Fe recovery	% Fe	% Fe recovery	Major constituent	Minor constituent	Trace constituent
XL1494	X9496	4061	P60-19-70A	0.051	1.22	2.68	56.7	82.6	-	-	Spinel	Wüstite (large)	Quartz (Hematite and pyrrhotite possible)
	X9497	4063	P60-19-70B	0.057	1.77	5.47	55.2	88.0	-	-	Spinel	Quartz (small)	Pyrrhotite (plus unidentified)
	X9498	4065	P60-19-70C	0.043	1.02	5.64	54.9	92.3	-	-	Spinel	Quartz	(Pyrrhotite and fayalite possible)
XL1495	X9499	4227	P60-19-70D	0.050	0.84	5.70	54.0	93.7	-	-	Magnetite	Hematite (large) Quartz (small)	Anhydrite (possible)
	X9500	4228	P60-19-70D	-	-	-	-	-	18.6	6.3	Quartz	Hematite Spinel Pyrrhotite (all small)	(Anhydrite, enstatite, possible)
XL1496	X9501	4229	P60-19-70E	0.058	0.76	5.38	53.3	88.0	-	-	Spinel Hematite	Quartz (small)	Anhydrite (possible)
	X9502	4230	P60-19-70E	-	-	-	-	-	36.4	12.0	Quartz	Hematite (large) Spinel (small)	(Anhydrite, feldspar, possible)
XL1497	X9503	4231	P60-19-70F	0.051	0.63	4.96	53.7	86.8	-	-	Spinel Hematite	Quartz (small)	(Anhydrite possible)
	X9504	4232	P60-19-70F	-	-	-	-	-	27.3	13.2	Quartz	Hematite (large) Spinel (small)	(Anhydrite, feldspar, possible)

The significant observations from these tables of X-ray results are:-

- (a) The major phase in the iron concentrates was a type of spinel, i.e., a phase having the formula $AO \cdot B_2O_3$, where A is a divalent metal ion such as Fe^{2+} , Mg^{2+} , Mn^{2+} , and B is a trivalent metal ion such as Fe^{3+} , Al^{3+} , Cr^{3+} . The value of the unit-cell parameter of the cubic spinel provides insufficient data to enable the composition of the spinel to be uniquely defined. In one case, so identified, the unit cell value was sufficiently near that of pure magnetite, $FeO \cdot Fe_2O_3$, that the material was specified as being this compound. In all other cases, the spinel phase could not be specifically identified, although it was obviously not far removed from magnetite in general composition. Included in the term "spinel" here is the compound γ -hematite, or maghemite, which is Fe_2O_3 in a magnetic crystal form analogous to that of Fe_3O_4 , but with 1 in every 9 iron atom locations vacant.
- (b) Small amounts of hematite usually remain in the various tailings and have thus not been reduced to a magnetic compound in calcination. This could

arise either from them not having been reduced to magnetite, or, alternatively, from a reversion of γ -hematite to α -hematite at the temperature of calcination.

(c) A certain amount of the iron persists through the calcination process as pyrrhotite, and is thus not available in a convenient oxide form.

(d) The quartz gangue minerals in the ore go, as one would expect, to the tailings in any magnetic separation.

(c) Chemical and Spectrographic Results

A semi-quantitative spectrographic examination of a head sample of the Algoma siderite ore in the Mines Branch laboratories gave the following results:-

Fe	-	principal constituent
Si	-	7.0%
Ca	-	4.0%
Mg	-	2.7%
Al	-	2.0%
Mn	-	1.7%
As	-	0.14%

The following elements were found to be present in amounts less than 0.1%, and, therefore, cannot be expected to contribute significantly to the reactions occurring on calcination:-

Ni, Cu, Pb, Nb, Zr, Ag, Na, Zn, Ta, Sr.

The following elements were sought, but in no case was any detectable amount present:-

Co, Mo, Cr, Ba.

The flotation concentrate of the siderite ore from the Helen Mine, produced with the object of cutting down the amount of arsenic and sulphur in the material, gave the following chemical analysis:-

Iron (as Fe)	- 37.2%
SiO ₂	- 1.64%
S	- 0.56%
As	- 0.022%
Mn	- 2.36%
Al ₂ O ₃	- 0.13%
CaO	- 1.45%
MgO	- 7.09%
P	- 0.13%

DISCUSSION OF RESULTS

From the complexity of the DTA and TGA traces, it is obvious that the calcination of the Algoma ore is a complex process, probably being the aggregate of a number of reactions, oxidative, reductive, or decompositional, involving a group of several minerals. In order properly to assess the results of the calcination and the nature of the products, it is necessary to elucidate the composition of the ore itself, and to consider the calcination behaviour of the constituent minerals.

The ore is predominantly a complex of mineral carbonates and may contain any or all of the following minerals:-

Calcite	CaCO_3
Magnesite	MgCO_3
Siderite	FeCO_3
Rhodocrosite	MnCO_3
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Ankerite	$(\text{Mg, Fe})\text{CO}_3 \cdot \text{CaCO}_3$

and intermediate products between almost any two or more of these individual minerals.

The thermal decomposition of this group of carbonate minerals has been studied extensively by J. Lawrence Kulp, Paul F. Kerr and their co-workers at Columbia University, New York (1, 2, 3). From their work, it can be seen that the approximate temperatures associated with the endothermic loss of CO_2 from the various single mineral carbonates mentioned above are as follows:-

Calcite	980°C
Magnesite	685°C
Dolomite	Two peaks at 790°C and 940°C
Siderite	580°C, followed by an exothermic peak when examined under oxidizing conditions.

(1, 2, 3) For References, see end of Report, Page 29..

Rhodocrosite 630°C, followed by an exothermic peak when examined under oxidizing conditions.

Ankerite Three peaks at 700°C, 840°C, and 910°C to 950°C.

The positions of these DTA peaks are, however, affected to a considerable extent by a) the presence of impurities, inert or otherwise, b) the state of division of the mineral, c) the precise experimental conditions of examination, d) the nature of the atmosphere under which the test is conducted, whether in air or in carbon dioxide, and e), of course, the extent of mutual substitution of the various metal ions involved. According to Kulp et al., complete ionic substitution appears to occur between the pairs Ca-Mn and Fe-Mg, whereas between Ca-Mg and Ca-Fe, however, the amount of substitution in a calcite-type lattice is very limited. Complete substitution between Fe and Mn, and between Mg and Mn appears possible, but is not completely represented in naturally-occurring carbonate minerals.

In addition to the complexities arising from the presence of several mineral species, and from the possibility of extensive inter-ionic substitution, one has also to allow for the interaction of the products of decomposition of the various species. For example, under oxidizing conditions, the iron carbonates can be expected to yield hematite, Fe_2O_3 , and/or magnetite, depending upon the oxygen partial pressure and the temperature. The magnesium carbonate would yield MgO. Interaction might then occur between

MgO and Fe_2O_3 to form $\text{MgO} \cdot \text{Fe}_2\text{O}_3$, magnesio-ferrite; this, in turn, could go into solid solution in the magnetite to give a complex spinel solid-solution product. As has been mentioned earlier, just such a material is observed as a major constituent of the calcination products. However, manganese, which is present in reasonably significant quantity, can also enter this spinel phase. Again, a further complication which has to be taken into account is the possibility of the formation of γ -hematite or maghemite. It has recently been shown by G.H. Hickie (4) that when ferrous oxalate dihydrate is heated in air, the intermediate product of the decomposition is γ -hematite and that, on further heating, an exothermic reaction occurs which is the conversion of γ -hematite to α -hematite. It is not at all unreasonable to expect that the ferrous carbonate (or siderite) decomposition would follow a similar pattern under oxidizing conditions. The temperatures of the reactions, however, would probably be markedly higher since the endothermic loss of CO_2 from FeCO_3 occurs at approximately 600°C , whereas the endothermic loss of CO and CO_2 from the oxalate occurs in region of 400°C . If γ -hematite is formed, it, too, can enter into the complex spinel phase since it has a defect spinel structure. This, however, may be only a temporary state of affairs since, at higher temperatures, it might revert to the α -form, which is hexagonal and could not form part of the spinel phase. This fact could account for the presence of some residual α -hematite in the calcined product.

Another observation made by Kulp, Kerr, et al., which may well be relevant to the present problem concerns the decomposition of ankerite. Ankerite is essentially a calcium-ferrous iron carbonate in which the ferrous iron is generally substituted by a certain amount of magnesium in such a way that the number of magnesium ions plus the number of ferrous ions is equal to the number of calcium ions. The decomposition of ankerite shows three endothermic stages. The first of these peaks is due to the decomposition of the carbonate ions most closely associated with the magnesium and iron positions. The products after this first stage are calcite (CaCO_3), MgO, and maghemite, the last being formed from FeO under oxidizing conditions. The magnitude of the second endothermic stage has been found to increase with the degree of iron substitution in the magnesium positions. It might be expected that this second endothermic peak was due to the formation of magnesio-ferrite, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$, from the constituent oxides. A consultation of tables of thermodynamic data will show that the formation of a double oxide, such as a spinel, from its constituent oxides is usually accompanied by a small thermal effect which can be either exothermic or endothermic, though more usually the former. However, in this case, the peak does not appear to be associated with magnesio-ferrite formation but rather, this second endothermic peak seems, according to Kulp, Kerr et al., to be due to the formation of a compound $\text{CaCO}_3 \cdot \text{Fe}_2\text{O}_3$. Experiments in our own laboratories have shown that a mixture of finely ground hematite

and calcite in 1:1 molar ratio produced the same peak as is observed with ankerite, and the product, when examined by X-ray diffraction, showed the presence of a material for which no published data are available, in addition to residual hematite and calcite. No concomitant weight change occurs during this reaction. Hence, if, during the commercial calcination of the Algoma ore, oxidizing conditions prevail, and the temperature of calcination is such that this second reaction of the ankerite decomposition can take place, but is not sufficiently high to result in the calcite decomposition and the consequent destruction of the above-mentioned addition compound, then a certain amount of the iron will be locked up as this $\text{CaCO}_3 \cdot \text{Fe}_2\text{O}_3$ compound, and will not be separable from the product by any magnetic method, either as magnetite, maghemite, magnesio-ferrite, or any solid solution product involving any or all of these, all of which are quite ferromagnetic in character. This would be a possible source of low recoveries in any magnetising roast under an oxidizing condition. The remedy for such a loss would be either the use of a strongly reducing condition, which would prevent the formation of the compound, or, alternatively, the use of a higher calcination temperature, which would result in its decomposition.

Having discussed the various possible reactions which could occur in such an assemblage of natural mineral carbonates, an attempt will now be made to assess, from the results quoted earlier in this report, the actual nature of the ore and the identity of the calcination products.

From the chemical and spectrographic data reported on page 13, from the DTA findings, and from the mineralogical study of the ore, it is known that siderite is by far the most abundant carbonate mineral present in the Algoma ore. It is of more interest to attempt to decipher the nature of the minor carbonate mineral constituents.

It will be seen that there is an endothermic peak at about 550-560°C, i.e., at a lower temperature than that given by siderite itself, which is in the region of 600°C. Now, from the data for the single mineral carbonates given on page 15, it will be observed that siderite gives a lower endothermic CO₂-loss peak than any of the other carbonates. The next lowest temperature is that of pure rhodocrosite, which is given as 630°C. It is considered that this 550-560°C peak is due to rhodocrosite, the temperature of the peak being depressed, partly by the effect of dilution by other materials, and partly by substitution of other ion(s) in the rhodocrosite lattice. According to Kulp et al., (2), "the temperature at which the endothermic peak (for rhodocrosite) appears depends on the amount of substitution of Ca, Mg, and Fe for Mn in the lattice, and, to a smaller extent, on the concentration of the mechanically admixed impurities present. Ca and Mg tend to raise the endothermic peak temperature because substitution of Ca or Mg for Mn strengthens the cation-carbonate bond, and, consequently, a greater amount of energy is required to destroy this bond. For analogous reasons,

substitution of Fe for Mn tends to lower the endothermic temperature". The presence of the very large amount of iron and the close similarity in ion size of Mn^{2+} and Fe^{2+} ($Fe^{2+} = 0.83 \text{ \AA}$; $Mn^{2+} = 0.80 \text{ \AA}$) renders the extensive substitution of this type very probable. The dilution by admixture also lowers the endothermic peak temperature. It is, therefore, felt that this 550-560°C peak is associated with the decomposition of a rhodocrosite constituent having extensive Fe^{2+} substitution for the Mn^{2+} .

Of the remaining peaks, occurring at temperatures in excess of 635°C, as listed in Table 2, only one is exothermic. This occurs at 740-760°C. In the CO_2 atmosphere, to which these data refer, the only reaction that can occur with evolution of heat is the reversion of γ -hematite, or maghemite, to α -hematite, and it is considered that this peak is due to this reaction, the thermal effect of which is known not to be large. The formation of some hematite by the decomposition of the siderite, rather than wustite, " FeO ", is, in all probability a result of the particular experimental arrangement used in our laboratories for DTA work. In this equipment, the atmosphere cannot be 100% CO_2 but must contain a small amount of air by diffusion effects; hence, some oxidation of the primary decomposition product of the siderite will occur. It appears that the product of this decomposition is γ -hematite. It is likely, therefore, that, in an oxidizing condition, γ -hematite would be the major primary product, which would revert, at higher temperatures, to α -hematite.

This is consistent with the very large, widely-spread exothermic peak obtained with the DTA examination of the ore in air over the range 640°C to 955°C, this peak resulting from the oxidation of the wustite, the first product of siderite decomposition, to γ -hematite, and from its subsequent conversion to α -hematite.

The various endothermic peaks occurring in CO_2 in the range 635°C to 1000°C+ are all associated with the decomposition of the other mineral carbonates. In order to account for all the peaks, it is necessary to postulate the presence of all possible carbonates. The endothermic peak at 680°C is attributed to the decomposition of magnesite. The endothermic peak at 1010°C is attributed to the decomposition of calcite. In view of the statement by Kulp, Kerr et al., (3) that "between Ca-Mg---the amount of substitution in a calcite type lattice is very limited", the diagnoses of the causes of these two endothermic peaks seem reasonably certain.

The moderate-sized endothermic peaks observed at 777°C and 936°C are attributed predominantly to the decomposition of dolomite, the lower peak being associated with the magnesium carbonate decomposition and the higher with the calcium carbonate.

The shoulder on the high-temperature side of the 680°C magnesite peak, the shoulder on the high-temperature side of the lower dolomite peak, at about 840°C, and a portion of the 936°C peak are attributable to the presence of ankerite in quite small amount.

Any attempt to assess the actual amounts of each of the carbonate minerals present would be thwarted by the fact that most of the metal ions concerned are partitioned between two or more species, e.g., the Fe between siderite, ankerite, and rhodocrosite, the Ca between calcite, dolomite, and ankerite, and the Mg between magnesite, dolomite, and ankerite. It is, however, obvious, from the magnitudes of the various DTA peaks and of the accompanying weight losses, that siderite is the main carbonate and is present in an amount approaching 60% of the head sample. The other mineral carbonates probably total about 15% of the head sample and are divided approximately equally between the various possible species, rhodocrosite, magnesite, calcite, dolomite and ankerite, with the iron-bearing rhodocrosite probably being the most abundant species and the ankerite the least abundant.

Turning now to the nature of the products of calcination, it is obvious that these will vary according to the temperature to which the calcination is carried, and the nature of the atmosphere, oxidizing, reducing or neutral, prevailing during the upper portion of the calcination temperature range.

The temperature that is customarily used in plant operation is about 800°C and the atmosphere is oxidizing rather than reducing. At such a temperature it is virtually certain

- (a) that the carbonate associated with magnesium ions will be decomposed to MgO.

(b) that the carbonate associated with calcium ions will not be decomposed but will remain as CaCO_3 to a large extent.

(c) that this behaviour will not be dependent on the atmosphere prevailing at the time of calcination, since Mg and Ca are uniformly divalent.

The products of the calcination of the other carbonates, rhodocrosite, siderite and ankerite, are rather less well-defined. In an oxidizing atmosphere it appears most likely that the primary product of calcination of siderite, being formed at a temperature in the region of 600°C , is maghemite or γ -hematite. At higher temperatures this reverts exothermically to α -hematite, but if some of the γ -hematite forms part of a spinel solid-solution product it is quite likely that this portion may persist in this form even at 800°C whereas most will have reverted to the α -form.

In the ankerite decomposition, as already discussed, at 800°C in an oxidizing atmosphere, the products appear to be MgO , calcite and the compound $\text{CaCO}_3 \cdot \text{Fe}_2\text{O}_3$. The extent to which the latter compound is present will depend on the precise local temperatures, since the figure of 800°C is right in the range of formation of this compound. Any local hot spots will result in its decomposition; any local cold spots will probably result in the constituents, CaCO_3 and Fe_2O_3 , remaining as such, and not

combining to give this compound. Since, however, the amount of ankerite in the ore is not considered to be large, this factor is probably not of great significance, except, as mentioned above, it could be a source of low recovery of iron in a magnetising roast.

The iron-bearing rhodocrosite, when calcined in an oxidizing atmosphere to 800°C, will, in all probability, yield a manganese ferrite, $\text{MnO} \cdot \text{Fe}_2\text{O}_3$, which would be magnetic and, thus, recoverable. The ferrite would also probably enter into the general spinel solid-solution phase since it possesses this structure.

From Table 3, page 10, it will be seen that the head sample of the calcined product contained 14.2% Fe in the ferrous state and 31.7% Fe in the ferric state and was shown to contain a major spinel phase, with traces of hematite and pyrrhotite. The pyrrhotite would account for some of the ferrous iron. The remainder would, presumably, be in the general magnetite-maghemite-ferrite spinel solid-solution. Since the amount of ferric iron is significantly more than double the amount of ferrous iron, this spinel phase must contain appreciable amounts of ferrites and/or maghemite in addition to magnetite, which would yield an exact $1:2 \text{ Fe}^{2+}:\text{Fe}^{3+}$ ratio. This is consistent with the above explanation of the decomposition products of the various carbonate species present.

The pyrrhotite observed as a minor constituent in the calcined product will have been formed by the decomposition of the small amount of pyrite, and/or arsenopyrite in the original ore.

The oxidation of the excess sulphur in the pyrite, FeS_2 , when heated in an oxidizing atmosphere is shown in the DTA work, as reported in Table 1, by the exothermic peak observed in the 419°C to 440°C range. This peak is, to a large extent, suppressed when the reaction is conducted in the protective CO_2 atmosphere, but may show to a slight extent due to imperfection of the protection from oxidation. In the flotation concentrate, designed to reduce the amount of sulphides and arsenides, this exothermic peak is much less evident when the concentrate is heated in air, and totally absent when it is heated in a carbon dioxide atmosphere.

Accepting all the above deductions concerning the nature of the ore itself and of the various possible calcination products, and reverting to the various DTA and TGA experiments listed on page 8, a discussion of which has been deferred until the present stage of the report, the following observations can now be made regarding the ore and fractions separated from it:-

- (a) The yellow material selected from the head sample consists very largely of siderite plus minor amounts of magnesite and dolomite; there is little evidence of the presence of rhodocrosite or of ankerite; calcite also appears not to be present.
- (b) The black material selected from the head sample appears to show the presence of ankerite and of rhodocrosite in addition to the above constituents

in the yellow material. Again, no calcite as such appears to be present. The sulphides appear to be very largely concentrated into this black material and virtually absent from the yellow.

- (c) The non-magnetic fraction of the flotation concentrate from the Helen Mine ore contains only a small amount of the sulphide(s), but contains all the carbonate minerals except calcite.
- (d) The sulphitic siderite selected from the head sample, contained, as was expected, much more pyrite than the head sample itself; also, the arsenopyrite was detectable in this material. There was some evidence that the rhodocrosite was present in higher concentration in this fraction than in the head sample itself, though this was only an isolated observation and may have been coincidental.
- (e) No significant new observations could be made from the other materials examined.

CONCLUSIONS

1. The Algoma siderite ore consists of a complex mixture of carbonates with siderite (FeCO_3) being the most abundant single mineral species. Lesser amounts of iron-bearing rhodocrosite, magnesite, dolomite, calcite and ankerite are present. The ore also contains small amounts of pyrite, arsenopyrite, and quartz.

2. The products of calcination of the ore will depend on the temperature and atmosphere in which the calcination is conducted.

3. The predominant calcination product is a complex spinel solid-solution that may contain magnetite, maghemite, magnesio-ferrite, manganese ferrite, etc.

4. A portion of the iron may be lost in non-magnetic forms in such a calcination by either (a) the formation of the compound $\text{CaCO}_3 \cdot \text{Fe}_2\text{O}_3$, or (b) the reversion of some maghemite (or γ -hematite) to α -hematite under oxidizing conditions.

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3. J.L. Kulp, P. Kent, and P.F. Kerr. "Thermal Study of the Ca-Mg-Fe Carbonate Minerals". American Mineralogist, Vol. 36, Nos. 9 and 10, (1951), pp. 643-670.
4. G.H. Hickie. "The Thermal Decomposition of Ferrous Oxalate Dihydrate and the Preparation of Forsterite-Fayalite Olivines". Internal Report MS-60-86, September 14, 1960, of the Mineral Sciences Division, Mines Branch, Ottawa.

(Appendices I to III
follow on pages 30 to 33)

NFHB:RHL:DV

APPENDIX I

ALGOMA ORE PROPERTIES DIVISION
of
The Algoma Steel Corporation, Limited

Sault Ste. Marie,
Ontario

November 8th, 1960

Dr. Bright,
Mines Branch,
Department of Mines and Technical Surveys,
555 Booth Street,
Ottawa, Ontario.

Dear Dr. Bright:

I wish to thank you very much for a pleasant and instructive visit with you. I found it intensely interesting.

You will recall our discussion as to what iron mineral we made when we roasted. We did not know whether we had formed magnetite or gamma hematite in our calcining tests.

Would it clarify the problem if we heated some calcine in an oxidizing atmosphere? Would an exothermic reaction then indicate that we had formed magnetite and the lack of any exothermic reaction indicate that we had formed gamma hematite?

All my very best wishes.

Yours very truly,

C.M. Beck,
General Manager.

APPENDIX II

C.M. Beck

November 8th, 1960

Dr. John Convey,
Director,
Mines Branch,
Department of Mines and Technical Surveys,
555 Booth Street,
Ottawa, Ontario.

Dear John:

I want to thank you and all your people for the very kind and patient reception I was given last week. Everybody was very interested and very co-operative. There was a keen appreciation of the urgency of our problem.

I was particularly interested in meeting Dr. Bright and getting a glimpse of what some of the new tools can do. I feel sure that what he and Dr. Eichholz are doing will be most useful.

At the risk of enlarging our work out of proper bounds might I ask this. We have done our work at Ottawa on 1/4" material. Would it be possible to predict theoretically the comparative time necessary to roast our material if it were 1 1/4", 4" and 24"? This last is really dreaming but one might be able to do the job underground prior to any crushing. There is no harm in dreaming, is there?

All my very best.

Yours very truly,

C.M. Beck,
General Manager.

APPENDIX III

Mineral Sciences Division,
A.T. Prince, Chief.

555 Booth Street,
Ottawa, Ontario.
November 16, 1960.

C.M. Beck, Esq.,
General Manager,
Algoma Ore Properties, Limited,
Sault Ste. Marie, Ontario.

Dear Mr. Beck:

I thank you for your letter of November 8th. We are very pleased that you found your visit to our laboratories of interest to you. On our part may we say that we found the discussion of your problems very stimulating, and we are determined to do all in our power to assist you to solve them.

You enquire concerning the nature of the iron mineral formed in your calcination process, whether it is magnetite or maghemite.

We have, on an earlier occasion, subjected both maghemite and magnetite to differential thermal analysis in an oxidizing (air) atmosphere. The materials used were very finely powdered materials of quite high purity. They were actually "Mapico" Pigment Samples supplied by Columbian Carbon Company of 380 Madison Avenue, New York, 17. We found that:-

1. Magnetite gave a fairly large exothermic reaction at 200-210°C, leading to the formation of γ -hematite or maghemite. This was followed at about 510°C, by another exothermic reaction of significantly lesser magnitude, leading to the formation of α -hematite (the normal non-magnetic form of hematite).
2. Maghemite exhibited only the upper of these two exothermic peaks, i.e., at 510°C approx., the product being α -hematite.
3. α -hematite exhibited neither exothermic peak.

4. All three samples exhibited a very small endothermic reaction in the range 680-690°C; the reason for this is not known for certain, but I suspect it may be associated with a crystallographic rearrangement of some type in the α -hematite.

Considering now the application of these findings to the specific problem posed by you in your letter, we would say that, if one takes some freshly calcined material, which has not had any chance to react with atmospheric moisture and/or CO_2 , and crushes this material finely and examines it immediately, then, if two exothermic reactions occurring at reasonably well separated temperatures, as indicated above are observed, then the calcine contains magnetite, whereas if only one exothermic reaction occurs, then it contains maghemite (or γ -hematite).

It is quite likely that the actual temperatures involved may not be very similar to those quoted above for our experimental conditions. However, the phenomena observed should be qualitatively similar.

You should also bear in mind the purely chemical approach to the problem, as discussed while you were in Ottawa. Thus, if you examine the calcined product for total iron and also for ferrous iron, giving thereby the ferric iron by difference, and you find that the ferric iron is more than two-thirds of the figure for the total iron, then you can reasonably assume that you have formed some maghemite. The nearer the ferric iron figure is to the total iron figure, the higher will be the proportion of maghemite to magnetite in the product. It must be remembered that these remarks apply only to the magnetic fraction of the product, since any α -hematite formed will be non-magnetic but would contribute to both the ferric and total iron figures.

I trust that these remarks will be of use to you in considering your problems. We are still actively engaged in studying the chemistry, thermochemistry and thermodynamics of the siderite roasting process and will report again to you at an appropriate time.

Yours sincerely,

Norman F.H. Bright,
Head,
Physical Chemistry Section.