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A Preliminary Investigation of Chromite

Lester C. Brown

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A PRELIMINARY INVESTIGATION OF CHROMITE

by
Lester C. Brown

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical
Engineering

Montana School of Mines
Butte, Montana
May 1947

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A PRELIMINARY INVESTIGATION OF CHROMITE

INTRODUCTION

Nature of Investigation

The purpose of this thesis was to study the effects of cryolite and a mixture of cryolite and aluminum oxide on a chromite concentrate with special reference to (1) their ability to break the bond between the ferrous iron and chromic oxide in the chromite; (2) their relative ability to dissolve the chromic oxide as compared to the ferrous iron; and (3) the effects of temperature on (1) and (2).

Chromite

Chromium was discovered as early as 1798, but it is only in recent times that uses have been found for the metal. It is widely diffused in the earth's crust but does not occur in the free state. It has been estimated that the earth igneous rocks contain .037% chromium. Chromium has a high luster, great resistance to corrosion and good electrical conductivity; it is harder than iron but is brittle in the pure state. Because of this brittleness no extensive use has been found for the pure metal³. Its main use is as an alloy with iron.

The chief producers of the world's chromium varied for years from country to country, but since the discovery of the large high grade deposits of New Caledonia and Rhodesia, these two have produced the majority of the world's supply. Only during the two great wars has this foreign supply failed to reach our markets.

Origin

The principal mineral for the supply of chromium is chromite. It has a variety of names: chrome ore, chrome ironstone ore, or chrome iron ore³. Chromite is a mineral of the spinel group, which have a general formula $R^*R_2O_4$ or $RO \cdot R_2O_3$. The species of the spinel group are characterized by isometric crystallization. The octahedron is the most common form of the isometric system in which the spinel group crystallizes. X-ray studies show that the members of the spinel group have the same isometric atomic structure. Some of the other minerals of the spinel group are: Spinel, $MgO \cdot Al_2O_3$; Gahnite, ZnO, Al_2O_3 ; Magnetite, $FeO \cdot Fe_2O_3$; Franklinite, $(Fe, ZnMn)O$; Beryllium aluminate, $BeAl_2O_4$.

Chromite is a compound of ferrous iron and chromic oxide and is usually considered as $FeCr_2O_4$. When of theoretical composition it contains 68% Cr_2O_3 and 32% FeO . The chromium iron ratio¹⁶ is about 65 to 35 or 1.86 to 1.

Chromite occurs in peridotite rocks, the serpentine derived from them forming veins or embedded masses. It is one of the earliest minerals to crystallize in the cooling magma. The large ore bodies are probably formed during the solidification of the rock by magmatic differentiation⁶. E. Sampson believes that although chromite may crystallize at a late stage as a magmatic mineral, a large portion passes into a residual solution capable of considerable migration¹².

Pure iron chromite is never found in nature. There is always more or less replacement of FeO by MgO , and Cr_2O_3 by Al_2O_3 or Fe_2O_3 . Where the FeO has been replaced by the MgO , the deposits are considered

high grade chromite deposits; but where the Cr_2O_3 has been replaced by Al_2O_3 or Fe_2O_3 , the deposits are considered low grade chromite deposits. All foreign sources can be considered high grade deposits, while the deposits of the United States and Canada are low grade which are high in iron.

Montana Chromite

The largest known chromite deposits in the United States are those in the Stillwell complex of ultra basic rocks in Stillwell and Sweetgrass counties, Montana. These deposits are of the high iron type. During both great wars these deposits were exploited due to necessity, but when foreign chromite again became available the work on these deposits stopped. The chromite concentrates which were produced during the last war averaged 41.45% Cr_2O_3 but were still too high in iron for peace time competition.

Chromite Uses

The bulk of the chromite consumed in the United States is used by the steel industry, the refractory industry, and the chemical industry, the ratio in the order named being 4, 3, and 1. Consumption of chromite in the United States in 1939 was 320,000 long tons, and in 1941 was 714,000 long tons. During the post-war years the consumption is expected to be between the 1939 figure and the wartime peak.

Specifications for Industrial Use

The steel industry⁷ for many years has used Ferrochrome in making chromium alloy steels. These steels may contain from 0.3 to 30% chromium. The Ferrochrome is a chromium iron alloy made by reduction of

chromite in the electric furnace. Since Ferrochrome is used for its chromium content and not its iron content, the object of the manufacturers is to produce a ferrochrome high in chromium and low in iron.

The practice of making ferrochrome⁷ in an electric furnace is said to recover iron 100%, with chromium recovery being slightly less. It is therefore evident that a high chromium to iron chromite is the desired raw material of the ferrochrome manufacture.

The steel industry⁷ through years of experience decided that a ferrochrome containing 62% to 70% chromium would best cover the needs of the industry, for the following reasons: (1) a higher chromium content is hard to dissolve, thus increasing the time per batch; (2) a high iron content means a greater cooling effect and greater cost; (3) anything which adds to the melting time adds to the chromium loss in the slag; (4) Ferrochrome also carries impurities which increase the slag, thereby decreasing the furnace capacity.

In recent years there have been two new methods⁷ used in making chromium alloy steels, both utilizing the low chromium to iron chromites. They are (1) Chrome X¹⁵ (2) Rustless Iron and Steel patent process⁷ of changing low chromium to iron chromite directly into the electric furnace making stainless steel. Very little is known of this latter process.

Chrome X is a brain child of Marvin J. Udy of Chromium Mining & Smelting Corporation Ltd., of Canada. "It is a mixture of ferrochrome, carbon and an oxidizing agent (Sodium nitrate) and is so compounded that it will react exothermically to produce molten carbon (high or low) ferrochrome when added to the molten steel bath. The amount of

heat produced is regulated in such a manner that the bath is neither chilled or overheated." *

The refractory industry uses chromite in the manufacture of refractories. These generally take the form of chromite bricks and cement used for lining in furnaces in metallurgical plants.

The specifications on chrome ore for the manufacture of refractories differ entirely from the specifications on chrome ore for use in either the chemical field or the metallurgical field. The latter two fields prefer an ore which is chemically active while the refractory industry finds this type of ore is useless; this industry requires an ore which is chemically inactive.

The gangue material is of no interest to the chemical or metallurgical field other than with regard to its effect on furnace burden, but it is of great importance to the refractory industry. The melting point of the gangue material in natural chromite ores is around 2300°F. to 2600°F., which is exceedingly low for a refractory material.

The general specifications⁷ for a refractory are: the Cr_2O_3 should be 30-35%; Cr_2O_3 plus Al_2O_3 should total at least 60%; MgO should be about 15%; Silica should be no more than 6%; CaO must not be more than 1%; FeO should not exceed 15% - however, the iron is not troublesome if it is not in excess of the spinel ratio. These specifications are subject to modification.

The chemical industry⁷ uses chromite to make chromate and pigment. The standard chemical grade of chromium ore contains 44% Cr_2O_3 , and

⁷Jdy, Chrome X and Our Chromium Problem, p. 54

in this ore a high chromium to iron ratio is not required. In fact, some authorities say that high iron ores are preferable because they are more easily decomposed than low iron ores.

Montana chromite is suitable for use in the chemical industry, but the grade of ore is low. This would be a disadvantage since it must be made available for proportionally less money per ton than imported ores.

ECONOMICS

The consumer of chromite naturally uses the ore which is the cheapest and most satisfactory for his purpose. It is therefore necessary that Montana chromites meet the specifications of the consumer, and in addition the product must be transported to the point of consumption and still be able to compete with foreign chromite. The cost of transportation⁷ is considered the most difficult single item by most investigators.

In order for Montana chromite to meet the specifications of the steel industry and the refractory industry, some method must be found to raise the chromium iron ratio of the concentrate. Making Chrome X and using Montana chromite ores as in the Rustless Iron and Steel Corporation patent are two potentialities.

The U. S. Bureau of Mines⁷ has found that one of the most encouraging experiments is a process for producing metallic chromium by electrolytic means.

REVIEW OF PREVIOUS LITERATURE

Selective Reduction

Selective reduction of a chromite is a means by which the chromium iron ratio of an ore can be raised. Essentially it consists of reducing the iron in the chromite and not the chromium. Udy¹⁶ states that in selective reduction of a high iron chrome ore, one should add sufficient lime to replace the FeO and give a highly basic melt and then smelt in an electric furnace. Under basic conditions employed almost any chrome ore will suffer decomposition and its FeO content will readily reduce before the Cr₂O₃.

The U. S. Bureau of Mines found that there is a selective reduction of chromite when roasted with carbon²¹. The requirements for such a selective reduction are: (1) a roasting temperature of at least 1200°C., (2) the use of fine size chromite, preferably all passing 65 mesh, (3) the use of fine carbon. Best results were gotten when the amount of carbon used reduced 30% of the chromium. The reduced iron can be removed by cold dilute H₂SO₄ with little loss of chromium.

Matte Smelting

The U. S. Bureau of Mines found that when chromite was smelted in the presence of pyrite a matte was formed having a higher chromium to iron ratio than the ore. The nature of the Fe-Cr-S system under smelting conditions is such that it would be difficult to achieve good recovery of the high ratio material¹⁹.

When chromite was smelted in the presence of copper sulphide, the matte formed had a high chromium to iron ratio. When an excess

of copper sulphide was used two layers of matte were formed, one being high in copper and low in chromium and iron while the other was high in chromium. Attempts to make a separation of top and bottom as in nickel were unsuccessful¹⁹.

Roasting and Leaching

Roasting of chromite to form a soluble chromate and then leaching the calcine is the method most used by the chemical industry. If $\text{Cr}(\text{OH})_3$, Cr_2O_3 or chromite is intimately mixed with any one of many metallic oxides or a compound capable of decomposing into an oxide, and if such a mixture is roasted, the chromic oxide reacts with the metallic oxide and oxygen to form a chromate. The amount of oxidation varies greatly with different oxides and with different conditions of temperature, pressure and physical state of the reacting mixture. This is shown in Table I¹⁸.

Table I

A		B	
Oxidation of $\text{Cr}(\text{OH})_3$ at 460°C . by oxygen at 12 atmospheres pressure		Oxidation of Cr_2O_3 by air at 900°C . at atmospheric pressure	
Reagent	Conversion Percent	Reagent	Conversion Percent
None	1.4*	None	Trace*
$\text{Fe}(\text{OH})_3$	1.2*	$\text{Fe}(\text{OH})_3$	Trace
$\text{Cu}(\text{OH})_2$	5.3	SiO_2	Trace
$\text{Mn}(\text{OH})_2$	9.5	Al_2O_3	Trace
CaCO_3	56.9	MgO	17.5
SrCO_3	63.0	CaO	70.3
BaCO_3	52.8	NaOH	90.4
$\text{Zn}(\text{OH})_2$	72.0	Na_2CO_3	91.7
$\text{Mg}(\text{OH})_2$	82.7		
PbCO_3	100.0		
Ag_2O	100.0		

* Probably due to a trace of alkali impurities

It can be seen from Table I that Cr_2O_3 alone is not oxidized by roasting and Fe_2O_3 , Al_2O_3 or SiO_2 do not promote oxidation. The oxides of silver and lead are 100% efficient, and those of the alkalis and alkali earth are also effective. Most of these reactions reverse at high temperature. PbCrO_4 decomposes at 600°C ., MgCr_2O_4 at 900°C ., and CaCr_2O_4 at 1000°C .

The U. S. Bureau of Mines in the roasting tests used lime with magnesia, sodium sulphate or sodium carbonate as reagents. These were mixed with Cr_2O_3 or chromite and roasted 16 hours. Some of the conclusions reached are as follows:¹⁸

Impurities in a chromite can effect the roasting and leaching operation, both physical and chemical. The impurities may consume the roasting and leaching reagents. They may have direct chemical or catalytic influence. Silica, alumina and magnesia dissolve and contaminate the liquor, silica being the greatest offender. Iron appears to react with lime to form ferrite but does not seem to have any effect on the reaction producing chromate. Magnesia appears to be beneficial or at least harmless.

The impurities may increase or reduce the fusibility of the calcine. In general lime, magnesia, and ferric oxide reduce the fusibility while alumina and especially silica are likely to form fusible compounds. A combination of several impurities may have more effect than the sum of their separate influences.

A soda ash and lime mixture gave the best conversion to a water soluble chromate. The leach liquor contained

less impurities. A roast using CaO or MgO produces an insoluble chromite of slate gray or brown color.

Best results are gotten when the calcine is wet with water at intervals during the roasting period. Constant rabbling and intimate mixture of reagents and chromite are essential. 850°C. to 900°C. was found to be the best roasting temperature.

Chromite behaves the same as Cr_2O_3 . Any difference noted was attributed to the fact that it is less finely divided and more dense, thereby giving less molecular contact with the roasting reagents.

Udy states, "On the addition of lime it appears that MgO in the silicate is replaced and in turn the MgO replaces FeO in the chromite. Increasing portions of lime then replaces the FeO in the chromite and the Al_2O_3 and finally there is a complete decomposition of the chromite. If the quantity of lime is controlled so that complete decomposition is not reached, there results a constituent approaching magnesium chromite ($\text{MgO}\cdot\text{Cr}_2\text{O}_3$) which crystallizes as an altered chromite of higher specific gravity than the original chromite of the ore and can be readily concentrated from the silicate portion by water concentration. This concentrate may have a chromium to iron ratio of 8 to 1 or more, and after acid treatment as much as 50 to 1."*

Chlorination¹⁷

A chloride metallurgy for chromium may be justified since the oxide forms are not susceptible to low temperature gaseous reduction.

*Udy, The Utilization of High Iron Chrome Ores, p. 204

It also furnishes a method by which separation and purification may be made.

Two known methods are available for chemical destruction of the spinel lattice: (1) treatment by a chlorination process and (2) treatment by an oxidizing roast. The alkaline fusion methods dissolve virtually all the silica and alumina while a chlorination process does not attack silica but instead converts both iron and magnesia in the ore to corresponding chlorides. It therefore suffers from similar disadvantages of increased use of reagents when using low grade ore.

In 1920 Venable and Jackson¹⁷ found that the separate oxides that may occur in chromite to be chlorinated are in the order Fe_2O_3 370°C., Al_2O_3 450°C., MgO 475°C., and Cr_2O_3 625°C. The temperatures given are those at which the reaction starts.

Yatlov and Papova¹⁷ found that chlorine reacts with all the oxide constituents of chromite simultaneously and the components are not effectively separated by fractional chlorination as claimed by some patents. Most investigators have found that the action of free halogen in the absence of a reducing agent could only produce free oxygen, but the action of free oxygen on the chlorides of chromium at a temperature below 1000°C. is entirely towards the formation of Cr_2O_3 .

In general the only way to maintain a reducing condition in the presence of free halogen is by the use of carbon monoxide, phosgene or the chlorides of sulphur. In the presence of carbon, chlorine reacts readily with chromite ores at 700-1000°C. for the formation of CrCl_3 . The chlorination was found to stop due to the CrCl_3 filling the pore space, thus preventing chlorine from contacting the ore.

Attempts to chlorinate direct in a liquid $MgCl_2$ medium showed almost no chlorination results on passing chlorine through a bath of fused $MgCl_2$ containing C and Cr_2O_3 in suspension. This is probably due to the fact that $CrCl_3$ is not appreciably soluble in the liquid, nor is the solubility of Cl_2 great. Therefore an accumulation of $MgCl_2$ thus retards a simple chlorination process. $MgCl_2$, due to its filling action, destroys the contact of gas with ore and carbon, and since it is not volatile at the low temperature used it will stop the chlorination process.

The use of carrier particles, especially those of silica, helps chlorination since the temperature used is above the transition temperature for α quartz. This probably produces many fine cracks, fissures or partial cleavages. These will act as a reservoir for the liquid $MgCl_2$, attracting it by capillary action and thus partly withdrawing it from the ore surface. Carrier particles thereby tend to keep the ore and gas in contact, which is a requirement for a continuous process.

A possible chloride metallurgy of chromite might be chlorination of chromite ores at a temperature high enough to volatilize the chloride formed and in cooling the vapors separate a fairly pure $CrCl_3$ which could then be reduced by H_2 at $800^\circ C.$ or by conversion to a chromate in an alkaline fusion with subsequent electrolysis in an acid solution.

The chromic chloride might also be dissolved in a fused electrolyte and by electrolysis produce chromium. Nees¹³ using a mixture of 475 g. $MgCl_2$, 500 g. $NaCl$ and 730 g. $CaCl_2$ in which $CrCl_2$ or $CrCl_3$ is dissolved and at a temperature of $600-700^\circ C.$ using 50 to 100 amp/dm² claims about 85% efficiency in depositing chromium.

The U. S. Bureau of Mines¹⁷ has decided that the fundamental theory of chlorination of a chromite ore is feasible on a laboratory scale, but whether it would be economical on a commercial scale is not known.

Galley⁹ has patented a process for the removal of iron from chromite. His process requires ore ground to -100 mesh and then treated with a stream of gas consisting essentially of Cl, CO and a diluent gas substantially free of hydrogen. At 600-900°C. the iron forms FeCl₃ and is volatilized. Little or no CrCl₃ is formed at this temperature.

Fused Electrolyte

Theory

Molten salts are good conductors of electricity, and their conductance is generally considered to be ionic. The conductance of a mixture of fused salts is approximately a linear function of the composition, which indicates that no reaction takes place on mixing. Goodwin¹⁰ believes electrical conductivity in a fused electrolyte is not unlike that which takes place in solution, the electrolytes being in a higher state of ionization.

The conductivity of fused salts increases almost linear with the temperature. At high temperatures this relationship is not exactly true since the conductance begins to lag. The effect of temperature can be accounted for essentially by its effect on the viscosity of the melt⁵.

Lorenz and Helfenstein¹ proved that Faraday's Law is valid for the electrolysis of molten salts. This is true when distorting

influences are not present. In molten salts, however, the following factors tend to decrease the yield at the cathode and, therefore, lower the current efficiency⁶:

1. Mechanical losses
2. Vaporization of the metal by the use of too high a bath temperature
3. Secondary chemical reactions at the electrodes
 - a. Formation of higher or lower compounds at the cathode
 - b. General secondary reactions
4. Metallic clouds or fogs
5. Recombination of the anodic and cathodic products which are brought together by stirring and diffusion
6. Anode effect

In general, however, current efficiency will increase with increased current density.

The decomposition voltage of fused compounds decreases with increase in temperature. This would mean that it is desirable to use a high temperature, but when all factors are taken into consideration it is found that the nearer the temperature is to the freezing point of the electrolyte, the higher the yield of electro-deposited metal.

Electrodeposition from a Fused Electrolyte

The deposition of a metal from a fused electrolyte is usually at a temperature above its melting point, i.e. aluminum, magnesium. This manner of deposition would probably be prohibitive in the case of chromium since its melting point is 1615°C.

The solid deposition of a metal from a fused electrolyte was studied by Aten, Denhartog, and Westenberg². They found that differences in temperature of cathode plate cause irregularities in the distribution of the deposit, the tendency being for the metal to redissolve from the hotter portions and build up on the colder portions. Cathodes that had a crystalline surface to begin with caused the deposited crystals to grow as a continuation of the crystals in the electrode. Polarization voltage was low and decreased with rise in temperature of the bath. The wide differences which exist between the structure of the metal when electrodeposited from aqueous solutions do not exist at the higher temperature of the fused bath.

The U. S. Bureau of Mines, attempting to deposit chromium from a mixture of molten salt and chromite, tried many salts, including calcium and sodium fluorides and chlorides. It was found that chromium metal could be deposited from several baths as a powder mixed with oxides. The most promising electrolyte mixture consisted of CaCl_2 to which 10% CaO was added. Tests showed this mixture would dissolve 7.5% Cr_2O_3 . CO and CO_2 were given off at the anode with little Cl_2 . The current density used was 25 amps/sq. in. The temperature was varied between 1050 and 1100°C. with a great variation in results²¹.

It can be seen from the above information that the function of a fused electrolyte is the same as an aqueous electrolyte, the function of the electrolyte being:

1. To dissolve the compound of the metal to be deposited.
2. To conduct an electric current.
3. To have a higher decomposition voltage than the dissolved compound at the conditions of electrodeposition.
4. Not to react with the deposited metal.

When the requirements for an electrolyte are applied to chromite, it can be seen that the greatest problem will be the control of the iron present. If iron is insoluble in the electrolyte, it will cause no trouble; if it is soluble, then a way or means must be found by which the iron will be prevented from depositing with the chromium.

The international critical tables and other literature were searched in an attempt to find some similarity between chromium and aluminum. The only similarity which seems to exist is that chromium in the trivalent state acts like aluminum and the fact that in chromite Al_2O_3 sometimes replaces Cr_2O_3 . With this in mind cryolite and a mixture of cryolite and Al_2O_3 were chosen to be investigated as possibilities for an electrolyte for chromite.

Cryolite is a compound of sodium and aluminum fluoride having the chemical formula Na_3AlF_6 . Its remarkable solvent power for alumina and its greater electrochemical stability are what make possible the present day aluminum industry.

Hall discovered that cryolite would dissolve alumina, but made the general observation that many other combinations of aluminum fluoride with the fluorides of sodium, potassium, lithium and calcium would dissolve alumina in substantial quantities and could be used as an electrolyte. This offers a means of usefully varying the fusibility, conductivity, density and other properties of the fused electrolyte⁷.

Pure sodium fluoride melts at about 990°C . and cryolite at 1000°C . There is a maximum in the freezing point curve corresponding to the mixture having the composition of cryolite. The addition of either sodium fluoride or aluminum fluoride to cryolite results in a lowering of the freezing point. With sodium fluoride a eutectic mixture is formed,

which contains 76% sodium fluoride and 24% aluminum fluoride or 40% sodium fluoride and 60% cryolite. The eutectic mixture freezes at 885°C. The addition of aluminum fluoride to cryolite rapidly lowers the melting point to a minimum of 685°C. at a concentration of 63% aluminum fluoride. Cooling curves of these mixtures up to 57% aluminum fluoride indicate the existence of another compound ($5\text{NaF} \cdot 3\text{AlF}_3$) which corresponds to the composition of the mineral chiolite.

The volatility of the mixture of cryolite with aluminum fluoride increases rapidly with increase of the aluminum fluoride content. Calcium fluoride when added to cryolite lowers the freezing point, and also increases the density of cryolite.

Solubility of Alumina in Cryolite

The freezing point of cryolite is lowered by the addition of alumina until a content of about 16% is reached. The freezing point temperature at this composition is about 935°C. Further addition of alumina rapidly raises the freezing point so that the saturated solution at 1000°C. contains about 21% of alumina. Solid alumina is more dense than cryolite, but the solution of alumina in liquid cryolite is lighter than cryolite without dissolved alumina at the same temperature.

Fedatieff and Iljinsky⁷ believe that when the melt contains sodium fluoride in excess of the cryolite ratio the solubility of alumina is appreciably increased. This is true up to a eutectic mixture (60% cryolite and 40% sodium fluoride) which is saturated with 20% alumina at about 890°C. Beyond this point the solubility of alumina decreases until it shows no solubility in pure sodium fluoride. When cryolite

contains aluminum fluoride in excess of the cryolite ratio, the solubility of alumina decreases. Chiolite dissolves about 10% alumina at 1000°C. Calcium fluoride also has a low dissolving power for alumina.

Electroconductivity

Arndt and Kaloss⁷ found that the addition of alumina to cryolite lowers the conductivity and the lowering was proportional to the amount added. Mixtures having sodium fluoride present in excess of the cryolite ratio show a slightly higher conductivity than cryolite.

Solubility of FeO in Cryolite

FeO is apparently soluble in cryolite, but no reference could be found which stated the degree of solubility. In the aluminum process, iron which is dissolved in the cryolite is deposited with the aluminum during the first part of the electrolysis. It can be assumed that any iron from the chromite which is dissolved by cryolite will deposit with the chromium; therefore the amount of cryolite soluble iron must be controlled before a desired product can be obtained.

EXPERIMENTAL METHODS

Chemical Analysis

A complete analysis of the concentrate used is given in Table II and shows that the chromium iron ratio is 1.47:1.

Table II

	wt. per cent
Cr ₂ O ₃	43.15
FeO	25.7
Al ₂ O ₃	12.2
MgO	1.6
SiO ₂	3.35

Methods of Analysis

The analysis for chromium was made as given in Low¹¹ with a few minor changes. The fusion with Na₂O₂ was made in a nickel crucible which was heated to a dull red heat. The fused product was dissolved in water, after which the solution was boiled gently for 10 minutes. The ammonium carbonate addition was omitted so that the nickel which reacted with the Na₂O₂ would be in an insoluble state. The solution was filtered and the residue saved for the analysis of iron. The filtrate was acidified with 1:1 HCl and an excess of 25 cc. of the acid added. Potassium iodine and starch were added and the solution titrated with sodium thiosulfate.

The residue to be analyzed for iron was dissolved in 1:1 HCl. Test lead was added and the solution boiled until all iron was reduced. The solution was then decanted and cooled to room temperature. Fifteen cc. of phosphoric acid restraining solution and three drops of diphenylamine indicator were added to the cool solution. The solution was then titrated with potassium dichromate solution.

Furnace Procedure

The general procedure used in conducting the investigation was to place the cryolite or cryolite and Al_2O_3 mixture in a graphite crucible. This crucible was then placed in the furnace and the charge allowed to melt. After melting, a weighed portion of ore, which had been preheated, was added to the molten charge. The time the molten charge and ore were left in the furnace was at first not important, but later a definite time period was used.

Upon solidifying, the charge was broken open and examined visually. In making the examination of the fused mass, color change was the only available means. Cr_2O_3 on heating can produce colors of red, yellow, brown or green¹². Cryolite or cryolite and Al_2O_3 after fusion have a dirty white color. Chemical analysis of the fused mass was made on the last five melts.

A muffle furnace was first used to melt the charge, but in this type furnace it was hard to produce similar conditions from day to day. In using the electric resistance furnace the time required to melt a small charge was too long. Best results were gotten by preheating the charge in the muffle furnace up to a temperature just below the melting point and then transferring it to the electric furnace where control over conditions was much better.

The electric resistance furnace used is a Hoskins Electric Furnace Type FC102 using 12 volts and 1000 amps.

EXPERIMENTAL RESULTS

Melt One

About 50 grams of cryolite were placed in a small fire clay crucible and allowed to melt in the muffle furnace. After melting, 2 grams of concentrate, which had not been preheated, were added. The addition was made in two stages. The second addition froze the charge. The furnace temperature was raised, and after the charge had again become liquid it was allowed to remain in the furnace for approximately one hour. Upon solidifying the fused mass was broken open and the following observed:

1. The top of the melt was covered with a light brown fused material which was soluble in HCl and upon addition of NH_4OH gave a white precipitate. It was therefore assumed that no iron was present.
2. The concentrate was found on the bottom and gave no visual appearance of the cryolite's ability to dissolve it.
3. Just above the concentrate the fused mass was colored a definite green. This color seemed to have moved upward from the concentrate.
4. Just below the brown cover, the mass was a dirty white color. This color extended through the top three-quarters of the fused mass. It indicated that the dissolving action of the cryolite on chromite had not progressed far enough to color the whole fused mass.
5. In the center of the melt a hole had formed. This hole was either a shrinkage hole or a gas hole formed by the action of the cryolite on the concentrate, since the mass was cooled in its original crucible.
6. The fire clay crucible showed that cryolite attacked and dissolved the fire clay, and it was therefore decided not to use this type.

Due to the green color above the concentrate and the dirty white color of the top portion of the melt, it is assumed that cryolite does

attack the chromite concentrate and the time allowed during this melt was not long enough to permit complete coloring of the fused mass. Because of the freezing of the melted charge after the second addition of concentrate, it was decided to preheat all concentrates before adding them to the liquid charge.

Melt Two

Fifty grams of cryolite and five grams of Al_2O_3 were charged to a graphite crucible and melted. Two grams of concentrate were preheated and added to the liquid charge in three stages. Approximately 15 minutes was the interval between the additions. After the last addition the crucible was left in the furnace for one and a half hours. It was then removed and cooled, and upon examining the fused mass the following was observed:

1. The top of the fused mass was covered with graphite which had broken away from the crucible.
2. Directly beneath the graphite cover was a thin green-colored layer of fused material.
3. The fused mass beneath the green layer was darkened. In the center was a hole whose sides were colored with a green similar to the top layer.
4. The concentrate was found at the bottom and showed very little evidence of attack by the mixture.

Because of the green-colored layer, the darkening of the fused mass, and the results of Melt One, it can be assumed that the mixture of cryolite and 11% Al_2O_3 , by weight, does attack the concentrate and it does dissolve some constituents or all of the concentrate. Part of the darkening of the fused mass was probably due to entrapped graphite particles.

Melt Three

Ninety grams of cryolite and ten grams of Al_2O_3 were melted in a graphite crucible and three grams of preheated concentrate added in five stages, 15 minutes apart. After the last addition the crucible was allowed to stay in the furnace for one hour. The temperature of the furnace was higher than for Melt Two. After cooling the fused mass was examined and the following noted:

1. Graphite top
2. Absence of green layer
3. The mass was a dirty white color.
4. The concentrate on the bottom showed no visual sign of attack.
5. Just above the concentrate the mass was colored brown, and, unlike the green color of Melt One, the color did not grade into the fused mass.

In regard to the appearance of the brown color, four other melts were made using the same type charge, but due to inability to duplicate furnace conditions, three of these melts gave the same appearance as found in Melt Two, while only in one did the brown color appear. When this melt was replaced in the furnace and remelted, the brown color could no longer be found, and to the eye it appeared the same as Melt Two.

The first conclusion drawn from these observations was that a higher temperature promoted a different reaction, and the brown color was believed to be a slag.

Upon then rereading the articles by Udy¹⁵ and the U. S. Bureau of Mines¹⁸, the writer believes the following to be true.

A higher temperature makes the melt more fluid and therefore the concentrate sinks to the bottom faster, the net result being that

the mixture would have less surface to act on and consequently in the same time interval there would be less visible evidence of the dissolving action of the mixture.

The brown-colored part of the fused mass is believed to be $MgCr_2O_4$. Udy¹⁵ states that on addition of lime it appears that MgO in the silicate is replaced and in turn replaces the FeO in the chromite. Increasing the portions of lime then replaces the FeO in the chromite. The U. S. Bureau of Mines¹⁸ states that $MgCr_2O_4$ is brown in color while $CaCr_2O_4$ is slate gray. The analysis of the concentrate shows that it contains 12.2% MgO and 1.6% CaO . A mixture of the two could account for the darkening of the fused mass.

Melt Four

The charge used was the same as in Melt Three with the exception that 10 grams of preheated ore were added to the liquid charge. Five additions were made with 15 minute intervals, and after the last addition the crucible was left in the furnace for two hours. Upon examination of the fused mass the following was observed:

1. Graphite top
2. Thin green layer beneath the graphite top
3. A greenish cast to the body of the darkened fused mass
4. The hole was covered with a brownish red dust. This could not be analyzed since it could not be collected.
5. The green color was more predominant just above the concentrate.
6. The concentrate which was left in the bottom showed green-colored inclusions.

This melt indicates that the coloring of the fused mass will vary with the amount of dissolved material. No explanation could be found for the reddish brown dust, but it might be Cr_2O_3 since it is sometimes red in color.

Because of the results in the first four melts, it seemed advisable to make a series of time temperature melts. These melts were first preheated in the muffle furnace and then placed in the electric furnace, which was set at 35 amperes. Higher amperage was tried, but at 45 amps the carbon crucible softened.

Melt Five

The charge consisted of 100 grams of cryolite and 7 grams of ore. The ore was placed on top of the cryolite and both preheated. After preheating the crucible was placed in the electric furnace where the charge melted. After melting it was left in the furnace for one-half hour and then removed and cooled. The following was observed:

1. Graphite top
2. Fused mass darkened
3. The concentrate at the bottom showed no visual change.

A part of the top of the fused mass was taken for analysis.

Melt Six

The fused mass from Melt Five was replaced in the crucible with the top down so that upon melting the concentrate would again pass through the cryolite. The charge was again preheated and melted as in Melt Five and then allowed to stay in the furnace for another half hour. Upon cooling the following was observed:

1. Graphite top
2. Very thin green layer of fused material below the graphite top
3. The fused mass was darker than at first, but no green color could be seen.
4. Less ore was visible at the bottom than after Melt Five.
5. The sides of the hole in the center were colored green.

This melt shows that cryolite and chromite will produce the green material as well as the cryolite Al_2O_3 mixture with chromite. The green-colored layer may be due to the Al_2O_3 content since the chromite concentrate does contain 14% Al_2O_3 .

A sample was taken of the green layer and of the darkened mass for analysis. The sample of the green layer was not too accurate since the layer was very thin and therefore it was impossible to obtain a true sample of it.

Melt Seven

The charge consisted of 90 grams of cryolite and 10 grams of Al_2O_3 , with 7 grams of ore placed on top of the cryolite, Al_2O_3 mixture. The charge was preheated and melted as in Melt Five, and left in the furnace one-half hour after melting. Upon examination the following was observed:

1. Carbon top
2. Fused mass uncolored
3. Concentrate at bottom

Apparently no action between the mixture and the concentrate had taken place; therefore no sample was taken for analysis.

Melt Eight

The fused mass from Melt Seven was placed in a graphite crucible with the concentrate up and remelted as before. After the charge melted it was left in the furnace for one half hour. Upon examination of the fused mass the following was observed:

1. Graphite top
2. Green layer below graphite top, thicker than the one found in Melt Six

3. The sides of the hole were colored green.
4. In the concentrate at the bottom was found a brown-colored streak. Green inclusions could also be seen in the concentrate.
5. The fused mass was darkened about the same amount as in Melt Five.

Apparently Al_2O_3 does have a great deal to do with the formation of the green layer since it seems to predominate when the Al_2O_3 content of the fused mass is raised.

The appearance of the brown color in the concentrate and not above as in Melt Three indicates that the brown color is probably soluble in the mixture, since in Melt Three it was found just above the concentrate, indicating that the color had moved upward and into the main part of the mixture.

Analysis was made on the green layer and on the darkened mass.

Melt Nine

The one remaining crucible was charged with 100 grams of cryolite and 7 grams of concentrate. The concentrate was mixed in the upper part of the charge and placed in the muffle furnace to preheat. In one half hour the crucible was found leaking so it was removed. Upon examination the following was observed:

1. Fusion had begun to take place around the sides of the crucible.
2. The portions of the cryolite which were in contact with the concentrate showed a definite color change. The colors found were yellow, orange, red and brown in different shades.

This indicates that intimate mixture of the concentrate and cryolite would speed up the dissolving action of the cryolite. It also indicates that a roast or longer period of preheating would have an increased effect on the action of cryolite on the concentrate. The

best temperature would probably be just below the melting point of cryolite or in the range of 900 to 1000°C.

Only the yellow and brown colors were analyzed since good samples of the red and orange were impossible to obtain.

Table III Analysis of Melts

Sample	Wt.-grams	Wt. Cr	Wt. Fe	CrFe Ratio (Fe = 1)	% Cr	% Fe
Concentrate	0.2000	0.0609	.0436	1.4	30.2	21.8
Melt 5 ($\frac{1}{2}$ hr) darkened mass	1.0000	0.00501	.0013+	3.78	.501	.13
Melt 6 (1 hr) darkened mass	1.0000	0.01001	.0028	3.85	1.0	.28
Melt 6 green layer	0.505	0.0026	.0018	1.44(?)	5.15	3.56
Melt 8 (1 hr) darkened mass	1.0000	0.0044	.0028	1.57	.44	.28
Melt 8 (1 hr) green layer	0.1597	0.0055	.0058	.95	3.44	3.63
Melt 9 yellow color	0.1739	0.0046	.0032	1.44		
Melt 9 brown color	0.1880	0.0022	.0014	1.57		
Melt 9 roasted ore	0.2020	0.0524	.0374	1.4		

On comparing the effect of cryolite with cryolite and Al_2O_3 mixture the analysis in Table III shows that for the same period of time and at the same temperature cryolite alone has a greater effect. It also shows that cryolite alone gives a larger chromium iron ratio. The cryolite, Al_2O_3 mixture chromium iron ratio is only slightly larger than that of the original concentrate.

If the Al_2O_3 is replacing the Cr_2O_3 in the chromite, the product formed (FeOAl_2O_3) is probably soluble in cryolite. By addition of AlF_3 , CaF_2 or NaF the solubility of Al_2O_3 in cryolite can be reduced. This might offer a way in which the FeO content of the cryolite could be controlled.

The analysis of the green layers shows that when cryolite is used alone the chromium iron ratio is very nearly that of the concentrate, while the chromium iron ratio in the cryolite Al_2O_3 mixture green layer showed a lower ratio. There was more of the green material formed when the cryolite Al_2O_3 mixture was used.

Miscellaneous Melts

Four other melts were made with the concentrate, using: (1) 475 grams MgCl_2 , 730 grams CaCl_2 , and 500 grams NaCl (Nees¹³); (2) CaCl_2 ; (3) NaCl ; (4) NaCl and cryolite. The first melt showed no action of the mixture on the chromite after being in the furnace for two hours. The second melt with CaCl_2 showed a gray color after being in the furnace for two hours. This is in agreement with the findings of the U. S. Bureau of Mines. NaCl alone showed no action on the concentrate, but the mixture of cryolite and NaCl showed a brownish color at the top. This color is believed to be due to the action of the cryolite and not NaCl .

CONCLUSIONS

Cryolite or a mixture of cryolite and Al_2O_3 does attack and dissolve the chromite concentrate. Cryolite alone acts faster than a mixture of cryolite and Al_2O_3 when both are used under similar conditions.

The action of Al_2O_3 with cryolite indicates that MgCr_2O_4 is soluble in cryolite and is one of the first materials to be dissolved. CaCr_2O_4 may be dissolved in the first stages, but due to its color it is impossible to determine this visually. Apparently FeOCr_2O_3 is harder to dissolve since the green color does not appear until after considerable time has elapsed. The action of Al_2O_3 in replacing Cr_2O_3 in chromite is believed to be the reason for the lower chromium iron ratio where using cryolite and Al_2O_3 .

Cryolite seems to have the ability to raise the chromium iron ratio during the first part of the melt. Whether this would be true when all the concentrate is dissolved is not known.

The green material formed may be a slag. Its formation is apparently increased by the addition of Al_2O_3 to the melt. Its chromium iron ratio is slightly lower than that of the concentrate.

RECOMMENDATIONS

In view of the fact that some of the above conclusions are based on the few time-temperature melts that were made, it is recommended that they be continued to determine the maximum solubility of Cr_2O_3 in cryolite and whether the chromium iron ratio changes with the increased chromium content. These melts should be made at a lower temperature, preferably a temperature at which the mixture is viscous enough to hold the chromite up in the melt. This temperature would be between 900 and 1000°C.

In view of the results obtained in Melt Nine, an investigation should definitely be made in which the effects of roasting cryolite with chromite are determined, the temperature range for roasting being between 850 and 950°C.

The effect of cryolite on MgCr_2O_4 and CaCr_2O_4 should be investigated, since it is known that chromite will break down when roasted with CaO or MgO , forming an acid insoluble chromite. This allows the iron to be removed, thus solving one of the problems connected with producing a salable product from a fused electrolyte.

The effect of decreasing the solubility of Al_2O_3 by adding CaF_2 , NaF and AlF_3 to cryolite should be investigated using a cryolite in which chromite has been dissolved. By controlling the solubility of Al_2O_3 , it may be possible to control the solubility of Fe , since Al_2O_3 is assumed to replace Cr_2O_3 in the chromite.

More finely ground material, preferably all passing a 100-mesh screen, should be used in any roasting or leaching operation to speed up the formation of the end product. Good mixing of the concentrate with reagents will also speed up and give better results in a shorter time.

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