

CHLORINATION OF CHROMITE WITH CARBON TETRACHLORIDE VAPOUR

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A method has been worked out for the chlorination of chromite with CCl_4 vapour, which can be used either for selective action on the iron constituent or for the complete chlorination of both iron and chromium.

Chlorination is inappreciable at 650°C . At 700°C ., the chlorination of iron is more pronounced, and best results are obtained in two hours when 80% of iron is chlorinated but only a third of the Cr_2O_3 is affected, the Cr/Fe ratio of the residue increasing to 10.64 (from 2.9 of the original ore).

Formation of CrCl_3 becomes pronounced from 750°C . Virtually complete chlorination of Cr_2O_3 (and, of course, FeO) can be achieved in three hours at 850°C . Silica remains unaffected.

Influence of several incorporates have been studied and the probable mechanism of the reaction discussed.

Introduction

Chromite is essentially $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, but may contain some magnesium and aluminium partly replacing iron and chromium, respectively. Varying amounts of silica are also present as gangue. The mineral has three major uses—as lining for refractory furnaces, for the production of chemicals, and for metallurgical purposes.

Tanning and electroplating industries are the largest consumers of chromium chemicals. These chemicals are produced either by alkali fusion or by acid treatment. The conventional alkali fusion consists of treatment with soda ash at high temperatures under conditions that allow the free access of air. Several modifications have been proposed.¹⁻⁴ Recently, electrolytic⁵ and aerial oxidation⁶ of chromite in fused carbonate melts have been successfully carried out. On broad principles, alkali fusion requires a low silica content of the ore and the iron is eliminated as insoluble ferric oxide. Acid treatment, on the other hand, requires an additional step for the elimination of iron, but a high proportion of silica is no more a problem. The acid treatment of chromite gained momentum from the beginning of the Second World War. Russian workers⁷ dissolved pulverized ore in 75% H_2SO_4 in the presence of manganese dioxide or chromic acid catalyst, removed iron by treatment with marble and crystallized out the chromium sulphate. A similar but elaborate process was reported by Gresford and Wylie⁸ and developed on a pilot plant scale by Clay *et al.*⁹ Other variations have also been reported.¹⁰

Although the metal has a high degree of resistance to corrosion, due to its brittleness chromium has so far been useful only for ferroalloys, which in turn has been obtained directly by reduction of

chromite. For this purpose, the ore should have low silica and a high Cr/Fe ratio. Low grade ores need concentration in this respect. Selective reduction¹¹⁻¹³ or selective chlorination¹⁴⁻¹⁶ of the iron constituent has been utilized for this purpose to a limited extent.

Recently it has been found that highly pure chromium (> 99%) is tough and ductile; this, together with the observation of unique properties of some chromium alloys, has focussed attention on the production of pure chromium either by reduction of the sesquioxide by aluminium or silicon, or more suitably by reduction of the pure chromium chloride by methods similar to those employed commercially with titanium. This has revived interest in the chlorination of chromite, but from a different objective, viz., the production of pure chromium chloride. Not much work has been done yet in this respect and only a few references are available. Thus Kroll¹⁷ has claimed the preparation of pure CrCl_3 by the chlorination of chromium carbide. Pokorny¹⁸ studied the chlorination of chromite elaborately (with Cl_2 and HCl) and noted that by briquetting with nearly an equal weight of coke, pitch and tar (10-55-25%) complete chlorination could be achieved at 800°C .

Qualitative study of the action of CCl_4 vapour on various oxygenated inorganic compounds had been made by Demarcay¹⁹ and Cambouives²⁰, but these workers have mentioned only the temperatures at which these compounds began to react. The possibility of utilizing this reagent had not been explored till recently. Niobium oxide²¹⁻²² and those of some transuranium elements have been chlorinated with CCl_4 . Pure violet CrCl_3 has been prepared by the action of CCl_4 on hydrated chromium sesquioxide,²³ but no reference has yet been made on the reaction

between CCl_4 vapour and the mineral chromite. The present paper summarizes the results that prove CCl_4 to be an efficient chlorinating agent for chromite. A short communication embodying some of the results has been published earlier.²⁴

Experimental

Description of Apparatus and Reaction Procedure.—The reaction was carried out in a silica boat placed inside a quartz tube ($24'' \times 1''$). The tube was heated in an electrically heated tube furnace, the temperature being controlled by means of rheostats and measured with a Pt/Pt-Rh thermocouple in conjunction with a Cambridge autocompensated indicator. The quartz tube was so placed inside the furnace that about 8" of it extended outside at the exit side. This side was connected through a ground joint adapter to a conical flask that served as a receiver for condensable vapours. This in turn was connected to another receiver that served as a check against back suction of strong alkali solution placed in the third receiver to absorb chlorine and carbonyl chloride etc. The exit gases, as a further safety measure, were passed through a small piece of silica tube and burnt by passing through a Bunsen flame.

The vapourizer containing the CCl_4 was connected to the inlet side of the reaction tube through nozzle. It had a narrow hard glass tube sealed centrally around its neck. This served for feeding the liquid at the beginning, and as it passed right down nearly to the bottom, it indicated the pressure of the CCl_4 vapour during the reaction. The vapourizer was placed inside a water bath maintained at $80 \pm 2^\circ\text{C}$. The feeding rate was controlled by watching the pressure change inside the central tube, which obviously was kept closed at the top during the reaction. The arrangement of the apparatus has been shown in Fig. 1.

An accurately weighed quantity of 100 mesh chromite ore was taken in the silica boat, and the

apparatus set up as described with the necessary connections. The furnace was now heated up to the desired temperature and kept steady there. The CCl_4 was brought to the correct temperature and feeding was started. This represented the beginning of the reaction, which was continued for a fixed period from this stage. After the reaction, the furnace was switched off and allowed to cool. The products in the receiver and in the exit end of the tube were taken together for analysis. The residue in the boat was also separately analysed.

Analytical Procedure.—For analysis of the ore as well as the unreacted residue in the boat, the sodium peroxide method of solubilization was adopted. In the residue, only chromium and iron were determined to obtain the Cr/Fe ratio. The ore, however, was completely analysed, and contained 40.3% Cr_2O_3 , 12.2% FeO , 16.2% Al_2O_3 , 6.9% MgO and 23.2% SiO_2 .

The volatile products of reaction were (violet) CrCl_3 , FeCl_3 , C_2Cl_6 , a little C_2Cl_4 and above 800°C . some small amounts of hexachlorobenzene and carbonaceous products; unreacted CCl_4 was also present. All these were taken up together by using water and some CCl_4 and a very little amount of HCl . The major amount of the CrCl_3 remained insoluble and was allowed to settle. The decanted liquid was separated into two layers. The CCl_4 layer was distilled to separate C_2Cl_6 and distil off CCl_4 (together with small amounts of C_2Cl_6 , if any); this can be reused. The residual violet chromic chloride was solubilized by treatment with a very dilute solution of sodium sulphite and some HCl . Slowly the violet insoluble mass turned green and dissolved in the aqueous medium. The solution was boiled to remove the sulphur dioxide and then mixed up with the aqueous layer obtained earlier from the separating funnel, filtered and made to a known volume. Iron and chromium were determined in aliquot parts by standard procedures.

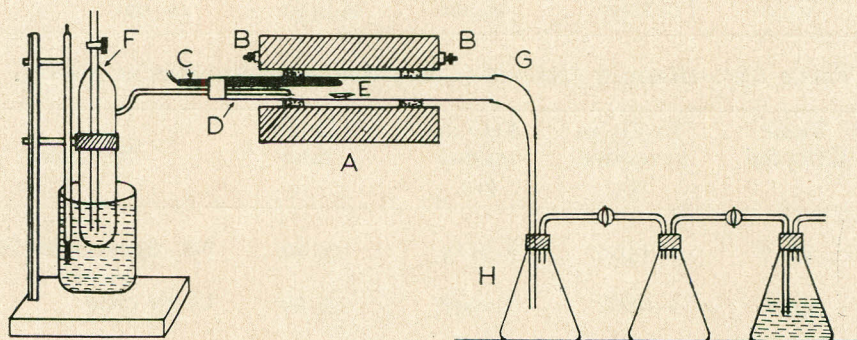


Fig. 1.—Electrically heated furnace with quartz reaction tube and vapourizer receiver flasks for chlorination of chromite with CCl_4 vapour. A Electric furnace; B. Terminals for connection; C. Thermocouple (within silica sheath); D. Reaction tube; E. Silica boat; F. Vapourizer containing CCl_4 and connected to reaction tube; G. Adapter with ground joint connection; H. Receiver flask.

Discussion

It is fairly well understood that the reactivity of a solid depends on its genesis. The recent work on chlorination of chromium sesquioxide by carbon tetrachloride²³ was performed with the hydrated compound, $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Apparently this was prepared by metathesis from solution, and such compounds are usually reactive. When the above work was repeated by the authors with a sample of ignited Cr_2O_3 , the latter remained virtually unaffected at 600-650°C. The natural chromite ore was expected to be less reactive than the ignited sample. Preliminary experiments with CCl_4 clearly indicated that the reagent is without any action on chromite at temperatures below 600°C. Further, the iron constituent in the chromite was found to be more reactive, and that temperature was the most important single variable in the reaction. Based on several exploratory experiments, final experiments were carried out at five different temperatures to ascertain the following:

(a) the optimum conditions under which the iron in chromite could be most selectively chlorinated, so as to leave a residue having a high Cr/Fe ratio (the original ore had 2.9);

(b) the lowest possible temperature at which the mineral could be completely chlorinated within a reasonable time, so as to produce a mixture of

iron and chromium chlorides. The problem of separating these from their mixtures will be discussed later on.

The silica content of the ore did not pose any problem, as it was observed that its conversion to the chloride would require much higher temperatures.

Reactions at Different Temperatures.—In all the experiments, the same amount of the ore (3 g.) was taken so that the results may be comparable. A number of experiments were carried out with varying space velocities, and it was found that under the present experimental conditions 20 ml. of CCl_4 per hour was quite convenient. The amount was quite in excess of that required for complete chlorination, even if only a part of the CCl_4 was consumed due to its decomposition, viz., $\text{CCl}_4 \rightarrow \text{C}_2\text{Cl}_6 + \text{Cl}_2$. At all temperatures different experiments were carried out by varying the time, and it was noted that the extent of chlorination did not improve with the feeding rate. Attempts were therefore made to keep the feeding rate between 20 ml. and 22 ml. per hour.

Results of reaction at 650°C. are presented in Table 1. Chlorination at this temperature was rather slow, but some chlorides were definitely formed. For both FeO and Cr_2O_3 , the chloride formation seem to take place from the beginning

TABLE 1(a).—ACTION OF CCl_4 VAPOUR ON CHROMITE AT 650°C.

Chromite taken 3 g. (corresponding to $\text{FeO} = 0.3660$ g. and $\text{Cr}_2\text{O}_3 = 1.210$ g.).
Rate of feeding $\text{CCl}_4 = 20$ -22 ml. per hour.

Duration in min.	Total CCl_4 fed (in ml.)	FeO reacted		Cr_2O_3 reacted		Remarks
		g.	%input	g.	%input	
60	20.0	0.0546	14.93	0.0610	5.04	Residue retained greyish colour
120	45.0	0.0720	19.60	0.1231	10.20	„
180	61.0	0.1063	29.00	0.1450	12.00	„

TABLE 1(b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

Duration in min.	Total CCl_4 fed	Cr_2O_3 in residue g.	FeO in residue g.	Cr/Fe ratio	Remarks
60	20.0	1.1490	0.3114	3.20	No appreciable change in
120	45.0	1.0869	0.2940	3.26	Cr/Fe ratio
180	61.0	1.0650	0.2597	3.61	

(Fig. 2) and proceeds slowly but steadily. In three hours, about 29% of FeO was chlorinated (to ferric chloride), while only about 12% of the Cr_2O_3 was converted into violet CrCl_3 . This temperature seemed to be rather low for complete chlorination, nor was it considered very effective for selective separation of iron.

Experiments at 700°C . produced the most fruitful results in respect of the selective removal of iron. Results given in Table 2 show that during the first hour, 32.4% of FeO reacted (29% in three hours at 650°C .), while 21.5% Cr_2O_3 also reacted (12% in three hours at 650°C .). The Cr/Fe ratio in the residue did not improve much (3.34, compared to 2.9 in the original ore), and the residual ore in the boat at the end of the reaction also retained the same greyish colour as that of the original. During the second hour of chlorination at 700°C ., the two constituents took altogether different turn. (Conversion of Cr_2O_3 into the chloride definitely slowed down (Fig. 2), whereas that for FeO was actually accelerated). As a result, at the end of two hours, 81.4% of the FeO was converted into ferric chloride, whereas only 31.8% of the Cr_2O_3 was chlorinated. The residual product in the boat was now greenish, indicating a concentration of Cr_2O_3 ; the Cr/Fe ratio increased to 10.64. Further continuation of the experiment for the third hour showed the same trend for chlorination of the Cr_2O_3 , only 38.10% being

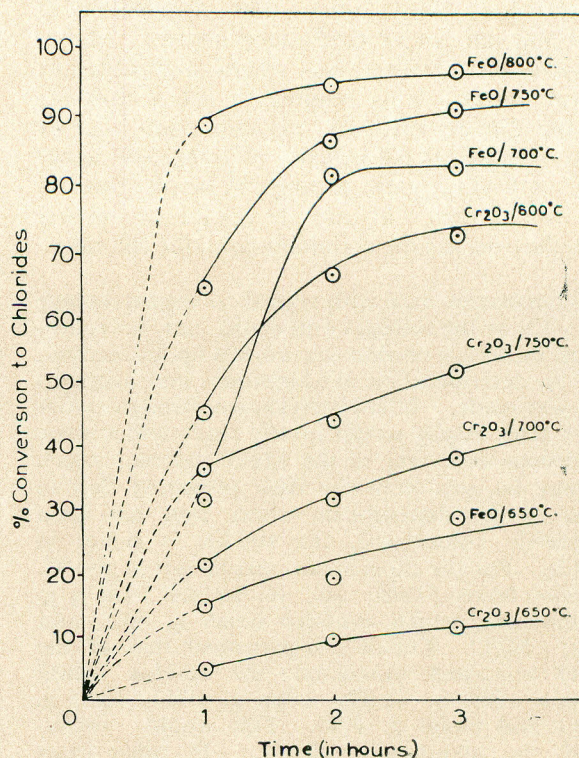


Fig. 2.—Progress of chlorination of chromite with CCl_4 vapour with time at different temperatures.

TABLE 2(a).—ACTION OF CCl_4 VAPOUR ON CHROMITE AT 700°C .

Chromite taken, 3 g. (corresponding to $\text{FeO} = 0.3660$ g. and $\text{Cr}_2\text{O}_3 = 1.210$ g.).
Rate of feeding $\text{CCl}_4 = 20$ - 21 ml. per hour.

Duration in min.	Total CCl_4 fed (in ml.)	FeO reacted		Cr_2O_3 reacted		Remarks
		g.	% input	g.	% input	
60	20.0	0.1186	32.40	0.2600	21.50	Residue more or less greyish
120	40.0	0.2980	81.40	0.3850	31.80	Residue turned greenish
180	62.0	0.2985	81.56	0.4615	38.10	„

TABLE 2(b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

Duration in min.	Total CCl_4 fed	Cr_2O_3 in residue g.	FeO in residue g.	Cr/Fe ratio	Remarks
60	20.0	0.9500	0.2474	3.34	Some change in Cr/Fe ratio
120	40.0	0.8250	0.0680	10.64	Considerable change in Cr/Fe ratio
180	62.0	0.7485	0.0675	9.76	„

converted in three hours. The chlorination of FeO also did not proceed much further. At this temperature therefore, best results were obtained in two hours. It is possible to get a chromite residue greatly enriched in chromium (Cr/Fe ratio over 10) at the expense of losing only about 30% of Cr₂O₃, while getting rid of the most of the iron content. It may be possible to recover both the iron and the chromium from the chlorides.

Quantitative data with regard to the percentage of Cr₂O₃ in the residual ores could not be collected as the entire residue was worked up for analysis, and no determination of aluminium and magnesium was made. It had been known through earlier work that Al₂O₃ would mostly react under these conditions and some of the MgO also may react. It may be seen from the data presented that in some of the experiments where iron has been selectively chlorinated, the residue is richer in Cr₂O₃. For the experiment carried out at 700°C. for two hours (Table 2b), we started with 3 g. of chromite, which contains 0.696 g. SiO₂ and 0.207 MgO. Even if it is presumed that all the MgO remained unreacted, the residue would contain 0.825 g. Cr₂O₃, 0.696 g. SiO₂ 0.207 g. MgO and 0.068 g. FeO. This would correspond to about 46% Cr₂O₃. In other cases when the main bulk of the Cr₂O₃ reacted, in any eventual industrial exploitation, the purpose

would obviously be to completely chlorinate Cr₂O₃ into the chloride.

Reactions at 750°C. (Table 3; also Fig. 2) follow more or less the same trend as those for 700°C. But as was quite expected, conversion of Cr₂O₃ to the chloride increased considerably—52% in three hours. Simultaneously, of course, the chlorination of FeO also increased—86.9% in two hours and 90.8% in three hours. From the point of view of chemical beneficiation, therefore, much better results were obtained at this temperature. The Cr/Fe ratio steadily increased in the residue and at the end of three hours it was above 15. This is a distinct improvement over all previous beneficiation methods; but, of course half of the chromium content of the ore is converted into the chloride (along with ferric chloride). At this temperature also, the chlorination of the chromium constituent is believed to be too slow for completion in a reasonable time.

A comparative study of the results in Table 4 with those for the preceding temperatures (Fig. 2) would clearly reveal that at 800°C., the extent of formation of chromic chloride in one hour (45.8%) is nearly the same as that for three hours at 750°C. (52.0%). In three hours, at 800°C., nearly three-fourths (73.6%) of the Cr₂O₃ was

TABLE 3(a).—ACTION OF CCl₄—VAPOUR ON CHROMITE AT 750°C.

Chromite taken 3 g. (corresponding to FeO=0.3660 g. and Cr₂O₃=1.210 g.).
Rate of feeding CCl₄=20-21 ml. per hour.

Duration in min.	Total CCl ₄ fed (in ml.)	FeO reacted		Cr ₂ O ₃ reacted		Remarks
		g.	% input	g.	% input	
60	20.0	0.2385	65.16	0.4400	36.42	Residue almost greenish
120	42.0	0.3180	86.90	0.5322	44.00	Residue turned greenish
180	61.0	0.3320	90.80	0.6295	52.00	„ „

TABLE 3 (b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

Duration in min.	Total CCl ₄ fed	Cr ₂ O ₃ in residue g.	FeO/in residue g.	Cr/Fe ratio	Remarks
60	20.0	0.7700	0.1275	5.28	Cr/Fe ratio changed
120	42.0	0.6778	0.0480	12.40	Quite a large improvement in Cr/Fe ratio
180	61.0	0.5805	0.0340	15.04	„

converted into the chloride. As was quite logical to expect, chlorination of FeO also increased; nearly 90% of it was chlorinated in one hour, but in three hours the ferric chloride formation was not entirely complete. It should be pointed out that one-hour chlorination at 800°C. produced nearly the same effect as that in three hours at 750°C. The comparative data is shown below:

Condition of chlorination	Vol. of CCl ₄ used (ml.)	FeO converted %	Cr ₂ O ₃ converted %	Cr/Fe ratio in residue
1 hr. at 800°C.	22	89.13	45.80	14.52
3 hrs. at 750°C.	61	90.80	52.00	15.04

Other effects being the same, the consumption of CCl₄ as well as the time is nearly one-third at 800°C. These conditions should therefore be preferred while preparing concentrates of Cr₂O₃, in case where the converted chromic chloride can also be simultaneously used or profitably disposed.

For the complete conversion of Cr₂O₃ to the chloride in a reasonable time, the temperature has to be further increased to 850°C. (Table 5). Under these conditions, 94.2% of the Cr₂O₃ was converted to the chloride in three hours; iron was also virtually completely chlorinated. In other words, at this temperature, chromite gives a volatile product comprising ferric chloride and violet chromic chloride. The residue contained very little of the corresponding oxides. It should be noted that at this temperature (850°C.), at the end of the experiment after three hours, the residue in the boat was snow-

white silica. This can be used as very pure silica raw material for various purposes. Also embedded in this silica residue were a few small pellets—believed to be the silicates of magnesium and aluminium formed from the oxides of these metals present as impurity.

The Chromium/Iron Ratio.—The Cr/Fe ratio of the residue at different temperatures have been plotted separately in Fig. 3. The curve for 650°C. is low and more or less linear. Curves for temperatures between 700°C. and 800°C. follow more or less the same trend, although the change with time is not linear. The maximum ratio achieved was 21.63 (3 hours at 800°C.), but considering other factors, the optimum ratio achieved was around 15 (1 hour at 800°C. or 3 hours at 750°C.). The curve for 850°C., particularly its latter portions, are a bit different—the Cr/Fe ratio decreases after passing through a maximum with the progress of chlorination. This shows that at 850°C. in the earlier stage, the progress of chlorination of FeO is the more prominent reaction, but after that the chlorination of Cr₂O₃ also proceeds steadily.

Effect of Incorporates on the Chlorination by CCl₄.—It has been seen in the earlier section that at 850°C, CCl₄ alone can convert chromite virtually completely into the chlorides of iron and chromium in a reasonable time. It was further noted that at lower temperatures a selective chlorination of the iron constituents take place. Thus at 700°C. the chromite can be considerably concentrated and in two hours the Cr/Fe ratio can be increased from 2.9 to 10.64. In achieving this result, a little over 30% of Cr₂O₃ is also converted

TABLE 4 (a).—ACTION OF CCl₄—VAPOUR ON CHROMITE AT 800°C.

Chromite taken 3.g. (corresponding to FeO=0.3660 g. and Cr₂O₃=1.210 g.).
Rate of feeding CCl₄=20–22 ml. per hour.

Duration in min.	Total CCl ₄ fed	FeO reacted		Cr ₂ O ₃ reacted		Remarks
		g.	% input	g.	% input	
60	22.0	0.3262	89.13	0.5540	45.80	Ash coloured residue
120	41.0	0.3474	94.90	0.8150	67.40	More or less white residue and few fused pellets
180	65.0	0.3530	96.40	0.8902	73.60	„

TABLE 4(b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

Duration in min.	Total CCl ₄ fed	Cr ₂ O ₃ in residue g.	FeO in residue g.	Cr/Fe ratio	Remarks
60	22.0	0.6560	0.1398	14.52	Large improvement in Cr/Fe ratio
120	41.0	0.3950	0.0186	18.68	„
180	65.0	0.3198	0.0130	21.63	Maximum Cr/Fe ratio

into the chloride form. Further concentration up to a Cr/Fe ratio of 15 to 20 may also be achieved, but at the expense of a larger amount of the Cr_2O_3 constituent being converted into its chloride. It was therefore necessary to explore whether through the use of any incorporate, the Cr/Fe ratio can be conveniently increased with a minimum of change of the Cr_2O_3 constituent.

The first incorporate tried was sodium chloride (Table 6), of which 1.0 g. was intimately mixed with 3 g. of chromite and the mixture used as the charge. Sodium chloride is known to influence many chlorination reactions in different ways. The authors had also seen in their earlier studies with sulphide minerals that sodium chloride behaved differently with different systems. In the present case, the sodium chloride retarded the chlorination of both the iron and the chromium contents, and rather advantageously from the authors' point of view—it also retards the chlorination of the chromium constituent to a greater extent. As a result there of, the authors obtained a slightly higher extent of concentration (Cr/Fe ratio 11.0, as compared to 10.64 without incorporates), but a relatively much lower percent of Cr_2O_3 (19.2% against 31.8% without any incorporate). This is a definite improvement, should one be interested in the concentration of the ore with reference to

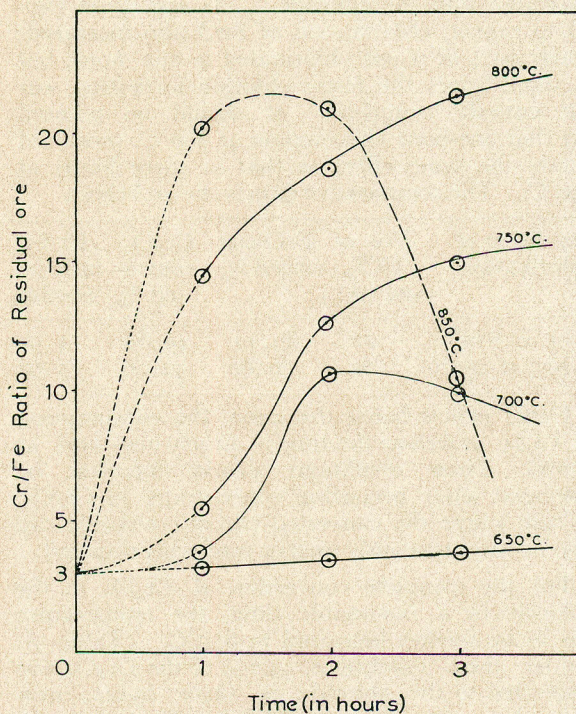


Fig. 3.—Variation of Cr/Fe ratio of the residual ore with progress of chlorination of chromite with CCl_4 vapour at different temperatures.

TABLE 5(a).—ACTION OF CCl_4 —VAPOUR ON CHROMITE AT 850°C .

Chromite taken 3 g. (corresponding to $\text{FeO} = 0.3660$ g. and $\text{Cr}_2\text{O}_3 = 1.210$ g.).
Rate of feeding $\text{CCl}_4 = 20$ – 22 ml. per hour.

Duration in min.	Total CCl_4 fed (ml.)	FeO reacted		Cr_2O_3 reacted		Remarks
		g.	% input	g.	% input	
60	21.0	0.3412	93.18	0.6392	52.85	Ash coloured residue
120	40.0	0.3530	94.40	0.8985	74.26	White residue embedded with some pellets
180	64.0	0.3601	98.40	1.1400	94.20	Snow-white residue also with few pellets

TABLE 5(b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

Duration in min.	Total CCl_4 fed	Cr_2O_3 in residue g.	FeO in residue g.	Cr/Fe ratio	Remarks
60	21.0	0.5708	0.0248	20.23	Large increase in Cr/Fe ratio
120	40.0	0.3115	0.0130	21.13	„
180	64.0	0.0700	0.0060	10.30	Both Fe and Cr in residue tend to zero concentration

chromium.

The effect of aluminium chloride was unfavourable. In fact, it changed the Cr/Fe ratio to 8.22. Aluminium chloride was used with a different purpose in view. It is known to react with ferric oxide and to give ferric chloride and aluminium oxide. Apparently, the reagent did not respond to ferrous oxide in the combined state in chromite. It should also be pointed out that aluminium chloride was used as an admixture with chromite and most of it volatilized out before the mass attained the reaction temperature.

With graphite and carbon the results were more unsatisfactory. In the presence of these incorporates much lower Cr/Fe ratio was found in the residue. This implies that proportionately lesser of iron was removed than chromium. In fact, the chlorination was clearly slow in the presence of these incorporates and only half of the iron volatilized as chloride. Graphite was used from ano-

ther point of view; it is known to form graphitic complexes with ferric chloride. Apparently such complexes were not stable at temperatures of 700°C. and above, because the volatile products on the exit side of the reaction tube contained both ferric and chromic chlorides.

Treatment of the Volatile Products of Reaction.—The products of chlorination were a mixture of anhydrous ferric and (violet) chromic chlorides, hexachloroethane and unutilized CCl_4 . Hexachloroethane can be easily extracted with hot CCl_4 and recrystallized. The excess CCl_4 can be reused. On a large scale, the mixture of the residual chlorides may be treated in either of the following ways:

(1) The violet chromic chloride is virtually insoluble in water, while the ferric chloride is readily so. A simple water treatment easily separates the two. The insoluble chromic chloride can be dried and finally volatilized in a stream

TABLE 6(a).—EFFECT OF INCORPORATES ON THE ACTION OF CCl_4 —VAPOUR ON CHROMITE.

Chromite taken 3.00 g. (corresponding to $\text{FeO}=0.3660$ g. and $\text{Cr}_2\text{O}_3=1.210$ g.);
Duration=120 minutes. Temperature=700° C.; Rate of feeding CCl_4 -vapour=
20-21 ml. per hour.

Incorporates	wt. of incorporate g.	Volume of CCl_4 fed (ml.)	FeO reacted		Cr ₂ O ₃ reacted		Remarks
			g.	%input	g.	%input	
None	—	40.0	0.2980	81.40	0.3850	31.80	
NaCl	1.0	42.0	0.2864	78.16	0.2323	19.20	Residue greenish
AlCl_3	1.0	41.0	0.2802	76.56	0.2542	21.00	„
Graphite	1.0	40.0	0.2001	54.64	0.1464	12.20	„
Carbon	0.50	40.0	0.1950	53.27	0.1343	11.10	Greenish black residue

TABLE 6(b).—RESIDUE ANALYSIS (CONDITIONS OF EXPERIMENT AS ABOVE).

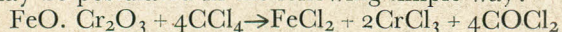
Incorporates	Vol. of CCl_4 (ml.).	Cr ₂ O ₃ in residue g.	FeO in residue g.	Cr/Fe ratio	Remarks
None	40.0	0.8250	0.0680	10.64	
NaCl	42.0	0.9780	0.0795	11.00	Most desirable Cr/Fe ratio
AlCl_3	41.0	0.9560	0.0860	8.22	Good Cr/Fe ratio
Graphite	40.0	1.0636	0.1650	5.67	Some increase in Cr/Fe ratio
Carbon	40.0	1.0760	0.1702	5.56	„

of chlorine or an inert gas, and finally reduced by magnesium.

(2) The solid mixture may be separated by high temperature differential volatilization. Alternately, the mixture can be treated with hydrogen in a gradually increasing temperature zone. Ferric chloride can be converted to the metal with the chromic chloride only partly changed to chromous chloride, which may then be treated for the production of chromium.

(3) Both the chlorides may be solubilized by treatment with water in the presence of a little sodium sulphite (this reagent is known to convert the violet chromic chloride into the water soluble green chromic chloride). Chromium may then be separated from the iron compound with the help of ion exchanger. Chromic chloride may be treated with sulphuric acid and the sulphate crystallized out for the tanning industry.

Mechanism of the Action of CCl₄.—The reaction may be postulated in the following simple way:



The actual mechanism appears to be much more complicated, as the above equation fails to explain the following:

(1) The equation postulates the formation of ferrous chloride, whereas actually all the iron was in the ferric form. The formation of ferric chloride as a secondary reaction can be explained only by presupposing the availability of chlorine from the decomposition of CCl₄.

(2) A simple equation as above would indicate the formation of the two chlorides in equivalent proportions. This would imply that the Cr/Fe ratio in the residue would remain unaltered, but we have seen that it does not only change but changes continuously.

The results cannot be fully explained by the direct action of CCl₄ on chromite. Although this may play some role at lower temperatures, complete chlorination of the chromite at 750°C. and upwards seems dependent on the decomposition of CCl₄ and the availability of nascent chlorine.

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