PELLETIZING AND CHEMICAL PROCESSING OF CHROMITE

Thesis
Submitted for the degree of
Doctor of Philosophy
in
The University of London

by

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December,
1962.

SYNOPSIS

This thesis is concerned with the beneficiation and agglomeration of standard grade chromite concentrate with low chromium:iron ratio by a sequence of processes including pelletizing of the finely powdered concentrate, selective reduction of the iron oxide by carbon and removal of iron by leaching with acid. Fundamental principles which control or influence the various stages of the process were examined and are appraised here.

A process of pelletizing fine chromite concentrate was evolved with a laboratory pelletizing drum. The following variables affecting the pelletizing process were investigated:

(1) Seeding of the load in the drum

(2) Moisture content of the feed and seeds

(3) Loading of the drum

(4) Drum diameter and drum velocity

(5) Rolling time.

The mechanisms deduced from these observations are discussed.

Sintering and reduction of the pellets were examined and the influence of various binding agents on this process was investigated. Reflected light microscopy and X-ray microradiography were used to elucidate the mechanism of sintering and to detect textural and mineralogical changes in the agglomerates. The

relationship between sintering temperature, amount of reducing agent incorporated and efficiency of removing iron by leaching are explained.

Acid leaching of the reduced pellets was investigated in respect of leaching rate, concentration of acid, temperature of leaching and quenching of hot pellets in acid at room temperatures. Optimum conditions for leaching are discussed.

Firing of pellets in a small, highly instrumented shaft furnace was attempted with combustion of town gas inside the stack. The distribution and geometry of temperature zones were plotted under various firing conditions.

ACKNOWLEDGEMENTS

The investigations presented in this thesis were carried out in the Mineral Technology Department of the Royal School of Mines, Imperial College of Science and Technology, London.

I wish to express my gratitude to Dr. E. Cohen for his valuable guidance, help and encouragement.

I am also grateful to the entire Mineral Technology staff of the Royal School of Mines for their invaluable suggestions and co-operation in this project.

Furthermore, I wish to thank the Malayan Government for sponsoring this project by the award of a Federal Scholarship.

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1.0 INTRODUCTION

Chromite is the only mineral occurring in sufficiently high natural concentration to form economical sources of the metal chromium for industrial uses. Deposits of chromite are mined in Rhodesia, Turkey, U.S.S.R., South Africa, India, Cuba, Yugoslavia, the Phillippines and many other countries. Crystallographically, the mineral belongs to the spinel group with an empricial formula of $FeCr_2O_3$ ($FeO.Cr_2O_3$). The FeO is commonly partially replaced by MgO and the Cr_2O_3 by Cl_2O_3. The unit cell of the crystal is a close-packed arrangement of 32 oxygen atoms. Half the trivalent metal ions are tetrahedrally surrounded by four oxygen atoms while the remainder together with all the divalent metal ions are randomly distributed and are surrounded octahedrally by six ogygen atoms[98]. The units are co-ordinated through the oxygen atoms to form one unit cell[97]. Chromite normally occurs in ultra basic igneous rocks and serpentines. A high grade ore may contain as much as 55% Cr_2O_3 with a chromium : iron ratio of 3.5:1, whereas, a low grade ore may have a Cr_2O_3 content of 20-40% and a chromium: iron ratio as low as 1.5:1.

The metal and the compounds of chromium are used for various purposes. Hard lumpy chromite rock is employed in the manufacture of refractories, particularly for basic open-hearth furnaces. Artificially prepared chromium salts find industrial

applications such as in paints, tanning, and chromium plating. By far the most important use of chromium is the production of ferrochrome for alloy steels. Although low grade chrome ores have recently been directly employed for the experimental production of chromium steel by the Wild's Process (1) (2) (3) and the "Chrom-X" Process (4) (5), standard grade ferrochrome is still the preferred basis for steel-making.

Metallurgical grade ore for the production of standard ferrochrome assaying about 70% Cr should contain a minimum of 48% Cr_2O_3 with a chromium:iron ratio of not less than 3:1. The material should be lumpy for easy handling and the amount of fines should be kept to a minimum to avoid unnecessary dust loss. Even in the refractory industry a chrome ore with less than 16% FeO and 6% SiO_2, and over 30% Cr_2O_3 is preferred.

High-grade ores conforming to these specifications are becoming increasingly rare, but there are very large reserves of low-grade chromite in Central and South Africa, India and many other parts of the world, mostly with low chrome:iron ratios of the order of 2:1. The iron does not occur in the ore as gangue but as a constituent of the chromite crystals. Conventional mineral dressing methods can therefore succeed only in improving the grade by removing the free gangue but fail to change the chromium:iron ratio. Various chemical methods have been tried for this purpose:

(1) Oxidation to chromate and reduction of chromate with carbon (6) (7)

(2) Leaching in sulphuric acid or alkali under pressure (7) (8).

(3) Leaching in sulphuric acid in the presence of chromic trioxide (9)

(4) Decomposition of chromite by alkaline fusion with silica and coke (Udy Process) (10).

(5) Partial or total chlorination at high temperatures (11) (12)

(6) Roasting under strongly reducing conditions and removal of acid soluble iron by acid leaching (7) (13) (14) (15) (16) (17) (18) (19)

None of these processes has been adopted by industry because of technical difficulties and economic inability to compete with natural products. A new approach to the problem is presented in this thesis.

It consists of the steps of forming fine chromite concentrates into pellets, heating the pellets in the presence of carbonaceous reducing agent whereby the iron in the chromite is rendered acid soluble and then removing the iron from the pellets by leaching with acid.

The specific advantages of this method may be summarised as follows:

1. Chemical advantages: porous pellets are more amenable to reduction than ores in lump or powder form. Leaching, washing and dewatering are similarly more efficient.
2. Physical advantages: pellets are superior to lump ores in constancy of physical and chemical constitution. They are preferable to fine concentrates in respect of handling and shipping qualities as well as in the reduction of dust losses.

2.0 PRESENT KNOWLEDGE OF REDUCTION ROASTING OF CHROMITE.

Chromite ($FeO.Cr_2O_3$) is a stable compound and does not decompose into FeO and Cr_2O_3 even at high temperatures. In the reaction:

$$FeO + Cr_2O_3 = FeO.Cr_2O_3$$

the free energy of formation (ΔF) is negative and becomes only very slightly less negative with rise of temperature (18) (see Table I). In view of this, the reduction of chromite cannot be regarded as a reduction of FeO in a mixture of ferrous oxide and chromic oxide.

TABLE I

Thermodynamic Values for the Reaction

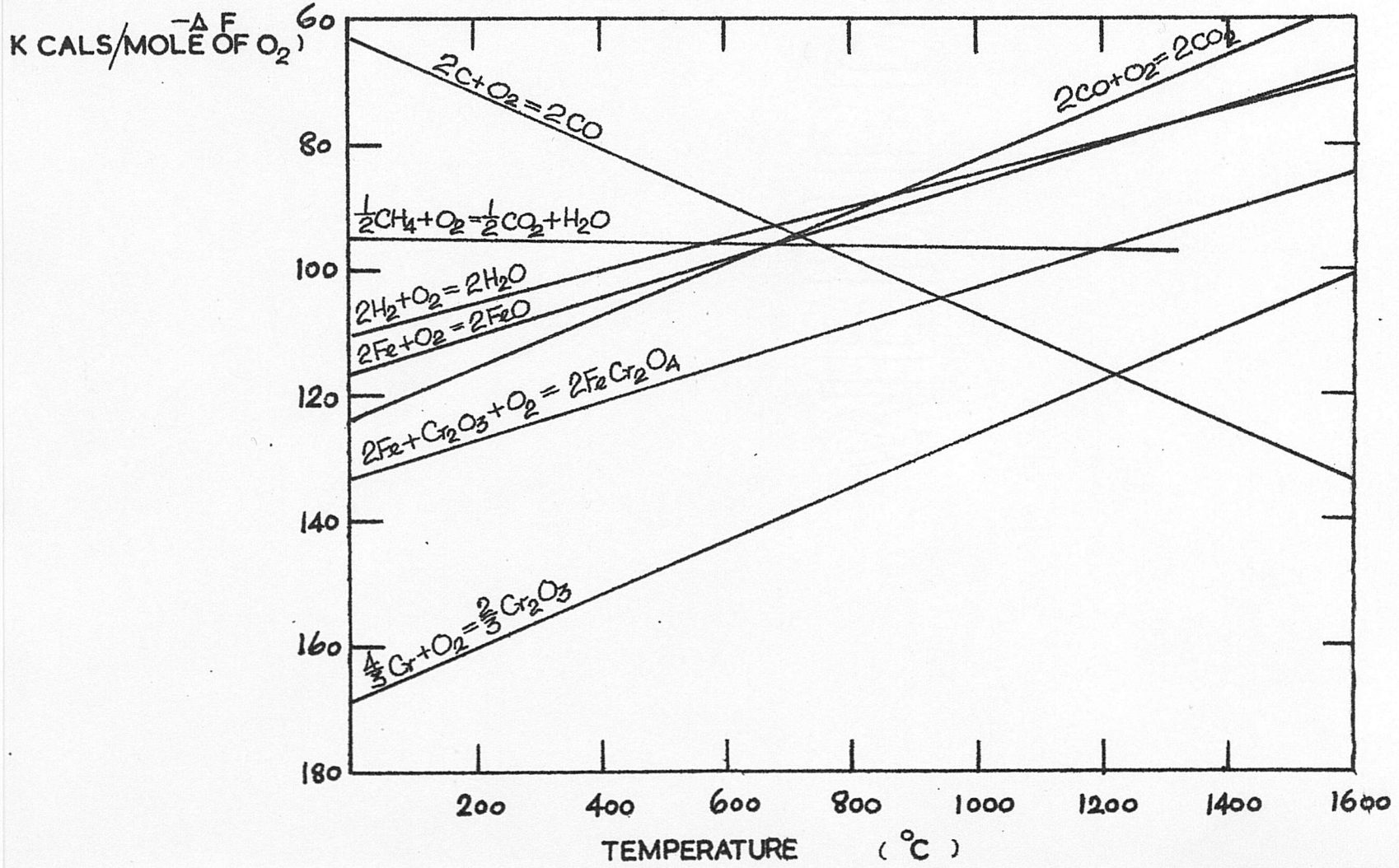
$FeO + Cr_2O_3 = FeO.Cr_2O_3$

Temp. in ^oK	Temp. in ^oC	ΔF
298.2	25.2	-8630
1000	727	-8500
1200	927	-8300
1300	1027	-8200
1400	1127	-8100
1500	1227	-8000
1600	1327	-7900
1700	1427	-7800

Kubaschewski and Evans (20) produced a chart showing the variation of the standard free energy of formation of oxides with temperatures (see Fig. 1). The values of the free energy of

FIG. 1

STANDARD FREE ENERGY OF FORMATION OF OXIDES IN THE REDUCTION OF CHROMITE



formation shown in the chart indicate that neither hydrogen nor carbon monoxide can be employed to reduce chromite. However, reduction can be carried out by using carbon or methane at about 950°C and 1150°C respectively. Furthermore, carbon will start reducing the chromic oxide at 1200°C. These thermodynamic considerations are based on the assumption that the chromite is reduced to metallic iron and chromic oxide, and that the gases produced are CO from reduction by carbon, and CO_2 and H_2O vapour from reduction by methane. The reduction of iron to iron carbides and the formation of CO and H_2 instead of CO_2 and H_2O from reduction by methane are not considered.

Boericke and Bangert (18) investigated thoroughly the equilibrium of the reduction of synthetic chromite by hydrogen, carbon monoxide, carbon and methane. They concluded that the reaction:

$$FeO.Cr_2O_3 + H_2 = Fe + Cr_2O_3 + H_2O$$

was slow below 1300°C and that only about 10% of the hydrogen would react at 1700°C. In using CO, C, and CH_4 for reduction, the following reactions were investigated:

(1) $FeO.Cr_2O_3 + C = Fe(\beta, \gamma \text{ or } \delta) + Cr_2O_3 + CO$

(2) $FeO.Cr_2O_3 + C = Fe(\gamma) + Cr_2O_3 + CO$

(3) $FeO.Cr_2O_3 + \frac{4}{3}C = \frac{1}{3} Fe_3C(\beta) + Cr_2O_3 + CO$

(4) $FeO.Cr_2O_3 + CO = Fe(\beta, \gamma \text{ or } \beta) + Cr_2O_3 + CO_2$

(5) $FeO.Cr_2O_3 + \frac{4}{3}CH_4 = \frac{1}{3} Fe_3C(\beta) + Cr_2O_3 + CO + \frac{8}{3} H_2$

The values of the free energy of reaction and their equilibrium constants were calculated. They are reproduced in Tables 2 and 3 below.

TABLE 2

Values of Equilibrium Constants of Reactions

$T^{o}K$	$T^{o}C$	K_1	K_2	K_3	K_4	K_5
1100	827	1.3×10^{-1}	1.3×10^{-1}	1.3×10^{-1}	All values very small	1.0
1200	927	7.4×10^{-1}	7.4×10^{-1}	7.8×10^{-1}		1.9×10^{2}
1300	1027	3.3	3.3	3.5		2.2×10^{3}
1400	1127	1.2×10	1.2×10	1.3×10		1.9×10^{4}
1500	1227	3.5×10	3.5×10	3.9×10		1.2×10^{5}
1600	1327	9.3×10	9.3×10	9.9×10		5.6×10^{5}
1700	1427	2.1×10^{2}	2.1×10^{2}	2.3×10^{2}		2.2×10^{6}

TABLE 3

Values of Free Energy of Reactions (cal./mole)

$T^{o}K$	$T^{o}C$	ΔF_1	ΔF_2	ΔF_3	ΔF_4	ΔF_5
1100	827	4,500	4,500	4,500	All values + ve	- 5,000
1200	927	700	700	600		-12,500
1300	1027	- 3,100	- 3,100	- 3,200		-19,900
1400	1127	- 6,900	- 6,900	- 7,100		-27,400
1500	1227	-10,600	-10,600	-10,900		-34,800
1600	1327	-14,400	-14,400	-14,600		-42,100
1700	1427	-18,100	-18,100	-18,400		-49,400

From the values of the free energy of reaction in Table 3, it can be seen that carbon can be used as a reducing agent at 1300°K or above and methane at temperatures as low as 1100°K. Carbon monoxide, however, is not an effective reducing agent. Consequently the gases produced during the reactions were expected to be CO and/or H_2.

On the basis of these thermodynamic considerations, investigations of the reduction of chromite using carbon and gases containing methane have been carried out by many workers (7) (13) (14) (15) (16) (17) (18) (19). It was found that the reduction reaction preferentially rendered the iron in the chromite acid-soluble. The iron could then be removed by leaching with sulphuric acid, leaving a residue with a high chromium:iron ratio.

Boericke (19) investigated the selective reduction of iron oxide in chromite by methane-hydrogen and similar gas mixtures, while Boericke and Bangert examined the reduction of chromite by graphite (13). Although the reaction temperature was found to be lower in gaseous reduction than in reduction by solids, as predicted by the thermodynamic considerations, difficulties were encountered owing to the cracking of methane which led to carbon deposition in the hot zone. The efficiency of methane as a gaseous reducing agent was thus lowered. Gaseous hydrocarbon was also found to exhibit comparatively poor selectivity in reduction, resulting in losses of chromium in the subsequent leach. Sen and

Chatterjee (16) used coke-oven gas containing 23% methane and 51% hydrogen to reduce low-grade Indian chromite and reported that the recovery of chromium was low. This was further supported by Misra, Sen and Bhatnagar (15) who reported a best chromium recovery of just less than 90% when Indian chromite was reduced with coke-oven gas for one hour at 1100°C. However, the chromium recovery fell to about 70% when the roasting temperature was increased in attempts to lower the roasting period. In general, for a fixed chromium recover, reduction by graphite gave a final product with a higher chromium:iron ratio than gaseous reduction; and for a fixed chromium:iron ratio, reduction by carbon produced higher chromium recoveries than reduction by methane-hydrogen mixtures(7). Carbon can, therefore, be considered as a better reducing agent than the gases.

Using carefully controlled small-scale laboratory tests, Boericke and Bangert (13) reported that the rate of reduction of fine chromite concentrate by powdered graphite was greatly affected by the roasting temperature. Reduction at 1200°C was ten times slower than at 1400°C. For all practical purposes a minimum roasting temperature of 1300°C was required. Roasting at high temperatures was also reported to have the added advantage of giving better carbon utilisation in reduction (13).

The amount of graphite used for reduction was also found to have direct effects on the proportion of acid-soluble

metal produced. For each ore there appeared to exist an optimum quantity of graphite addition. Beyond this, only slight increases in acid-soluble iron were obtained and chromium losses greatly increased. During the testing of low-grade domestic American chromite, the optimum graphite required for reduction was found to be between 4-5% by weight. This value was not greatly affected by the Al_2O_3 content of the ore. Hot sulphuric acid leaching after reduction by carbon was found to yield a high-grade leached residue with a chromium:iron ratio of 4:1 and a chromium recovery of +96%. Over 70% of the iron in the chromite could be leached out and in some cases 90% of the total iron was reported to have been removed.

However, the roasting period required for reduction was prohibitively long. One hour was required to roast one type of ore at 1300°C while 6 hours were needed in another instance. This roasting period could be reduced slightly by using chromite of finer sizes and chromium losses were also improved. In the interest of efficient and rapid reduction of chromite, Boericke and Bangert (13) recommended a maximum particle size of 65 mesh for ore and carbon.

The Hudson Bay Mining and Smelting Co. (7) used this method in modified form for treating fine material (80% - 325 mesh) with fine coal (90% - 200 mesh). It was found that the ore could be up-graded by hot acid leaching to a chromium:iron ratio of 3:1 with a chromium recovery of just under 95%. Contrary to the

findings of Boericke and Bangert (13), these authors required a minimum addition of fine coal of 20% (by weight). This frequently produced a residue of unreacted coke which caused undesirable frothing during leaching with boiling sulphuric acid.

A prohibitive roasting period of 2 - 3 hours at 1150°C was also experienced. An attempt to reduce the roasting period by increasing the temperature was found to reduce both the chromium recovery and the amount of acid-soluble iron. No explanation was given for this phenomenon.

Carbon reduction and acid-leaching were also adopted by Lloyd and co-workers (14) to beneficiate low-grade Montana chromite in a pilot plant by roasting it with 18-41% coke in a rotary kiln at 1340°C. The calcined material was leached in lead-lined pachukas with 10% (by volume) sulphuric acid at almost boiling temperatures. The up-graded ore was reported to have a chromium: iron ratio of over 3:1. Chromium recovery was high, but the final concentrate was contaminated with unreacted coke.

Difficulties were experienced with the rotary kiln for reduction. Owing to the large difference in specific gravity of coke and chromite, there was little mixing between the two materials and the coke tended to stay on top of the charge, Accretions of fine ore were also found to form on the kiln-wall in the hot zone and this became serious when the temperature was raised to 1410°C

Although simple in principle, this process proved uneconomical owing to the excessive roasting period and high coal-consumption. Downes and Morgan (7) considered that the process would not be cheap enough to encourage exploitation of U.S. ores under normal conditions, but it was believed to be quite satisfactory to meet temporary requirements in times of emergency.

3.0 CHOICE OF PROCESS.

The work described in this thesis was concerned with the development of a process which is technically and economically more attractive than its predecessors. The work was also aimed at an appraisal of the fundamental principles which govern the various stages of such a process.

Since selective reduction by carbon takes place in the form of solid-solid reaction, it was considered that pelletizing would improve the speed and efficiency of the process through the provision of intimate contacts between very fine chromite and carbon particles. The green pellets would be fired to high temperatures with the carbon in situ, sintering and reduction taking place simultaneously.

The fired, porous, product should offer easy leaching of the acid-soluble iron and facilitate washing and subsequent dewatering.

The present approach is, therefore, based on the following sequence of processes.

(1) Pelletizing of finely ground chromite concentrate with an appropriate carbon addition.

(2) Hardening and reduction of the pellet at high temperatures in a vertical shaft furnace.

(3) Removal of acid-soluble iron from the fired pellets by acid-leaching.

4.0 EXPERIMENTAL MATERIAL.

The chromite used in this investigation, obtained from the properties of Rose Chrome Ltd., came from the Great Dyke of Southern Rhodesia, east of Gwelo. Examination of the ore showed that it consisted of masses ofsmall grains of chromite embedded in a matrix of serpentine (serpentine - hydrous magnesium silicate $Mg_6Si_4O_{10}(OH)_6$), with small amounts of olivine (olivine - magnesium iron orthosilicate $(Mg,Fe)_2 SiO_4$). The average specific gravity of the serpentine is 2.6. Intimate intergrowths of gangue and chromite were common.

In order to obtain a high-grade final product from the process, excessive gangue material had to be removed. For this purpose a pre-treatment concentration process was essential. The ore was amenable to conventional methods of grinding and gravity concentration (tabling), and these processes were used in preliminary preparation of concentrates as feed for the subject of this thesis.

The concentrates, being -20 mesh BS in size, were too coarse for pelletizing and were further ground to -150 mesh BS. with about 50% -200 mesh BS. All fine particles were carefully recovered and the ground product was dried. Iron particles acquired during the process of grinding were removed on a "Rapid" high-intensity magnetic separator.

This treatment produced a concentrate which assayed

48.3% Cr_2O_3 (33.2% Cr)

20.3% FeO (15.8% Fe)

with a chromium:iron ratio of 2.1:1. The average specific gravity of the concentrate was 4.17 and the specific surface area, as determined by the air permeability method, was 2,000 sq.cm/gram. The size distribution of the material was determined by screening and beaker decantation and is shown in Table 4.

Table 4.

Size Distribution of Ground Chromite Concentrate

SIZE		DISTRIBUTION	
BS. Mesh	Microns	%Wt. Direct	Cum. % Finer
+100	+152	2.9	97.1
+150	+105	10.1	87.0
+200	+ 76	39.8	47.2
	+ 53	31.5	15.7
	+ 38	3.1	12.6
	+ 30	3.7	8.9
	+ 20	3.3	5.6
	+ 10	3.7	1.9
	+ 5	1.3	0.6
	- 5	0.6	
Unsized		100.0	

Examination of the sized fractions showed that the particles coarser than 30 microns are granular and rounded. Many of them are locked middlings, consisting of chromite with inclusions of fine gangue minerals. The amount of middlings

decreases with particle size, but full liberation of chromite is only attained at about 30 microns. Particles of this order of size are angular, having sharp edges and pointed corners.

Study of polished sections of chromite grains (Plate 1) showed that the grains are full of veinlets and hair-cracks which occasionally lead to cavernous interiors. These spaces had probably been occupied by soft gangue material which was lost in preparing the specimen.

The chromite crystals exhibited no visible intergrowths of magnetite, zoning or other heterogeneities.

X-ray powder diffraction patterns of the concentrate were also prepared, using cobalt radiation. The lines obtained corresponds to those of chrompicotite $(Mg,Fe)\ O\ (Cr,Al)_2O_3$ as reported in the A.S.T.M. index. The three prominent lines correspond to 2.3Å, 1.59Å and 1.46Å.

A scan of the X-ray fluorescence spectrum of the concentrate was carried out with a Raymax 60 spectrograph. This showed chromium and iron as the only heavy elements present, the limit of detectability being about 0.05% for elements of atomic weight greater than 50.

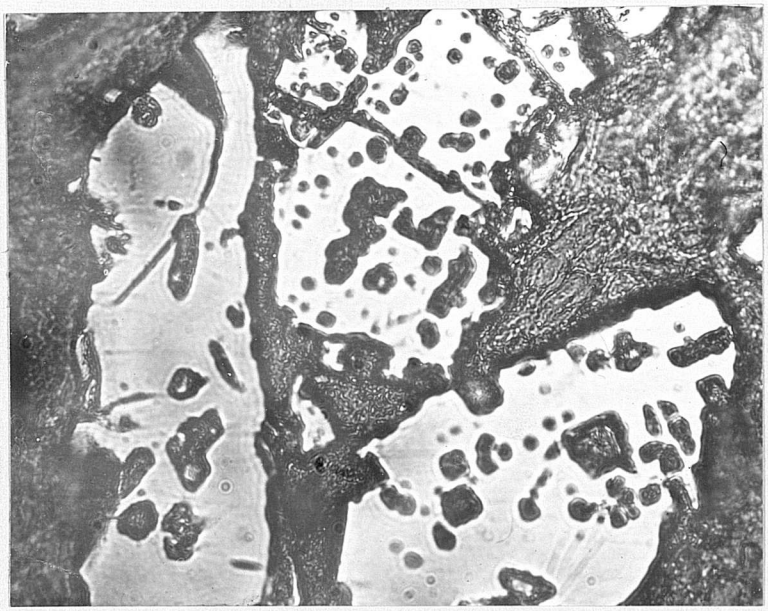


PLATE I.

Polished Section of Untreated Chromite.

(×570)

5.0 AGGLOMERATION

5.1. Introduction.

"Pelletizing" - the agglomeration of fine material into spherical pellets by rolling was first introduced into the mineral industry by A.G. Andersson (21) in 1911, in Sweden, where he successfully pelletized fine iron ore in a rotary drum. His work was not appreciated and the process was soon ignored. Later Brackelsberg (22), Barrett (23) and Dean (24) independently developed similar methods offorming iron-ore pellets. Pelletizing then gradually became accepted in the mineral industry as a process of agglomeration, simple in principle and economical in operation.

In pelletizing, a finely powdered material, together with a certain amount of moisture, is fed into a horizontal, rotating drum or into other revolving vessels where balling occurs. The spherical pellets thus produced are continuously discharged, as a product showing a range of sizes. Pellets considered too small for subsequent treatment are removed by screening and returned to the feed of the machine. The small pellets mix with the new feed and act as "seeds" in the agglomeration process. The pellets in this way increase in size and are eventually discharged as finished products, while undersize material may be returned repeatedly to the feed of the process. This forms a circulating load which may amount to several hundred percent of the fresh feed.

The material to be pellitized can be either wet or dry and water sprays are often used in the pelletizing machine if

insufficient moisture is present in the feed. A scraper to clean the wall of the machine is generally needed to avoid excessive accumulation of the wet material.

Generally, high rates of through-put can be achieved by this process. Holly and Apuli (26) reported a through-put of 50 tons of ½ inch iron-ore pellets per hour from a 9' x 30' drum, while Davis and Wade (27) successfully pelletized magnetic taconite in a drum (whereas briquetting was excessively expensive owing to high power consumption and die wear).

Although this process of agglomeration is now being widely practised, its fundamental mechanism is still obscure and little work on the theory of pelletizing has so far been published,

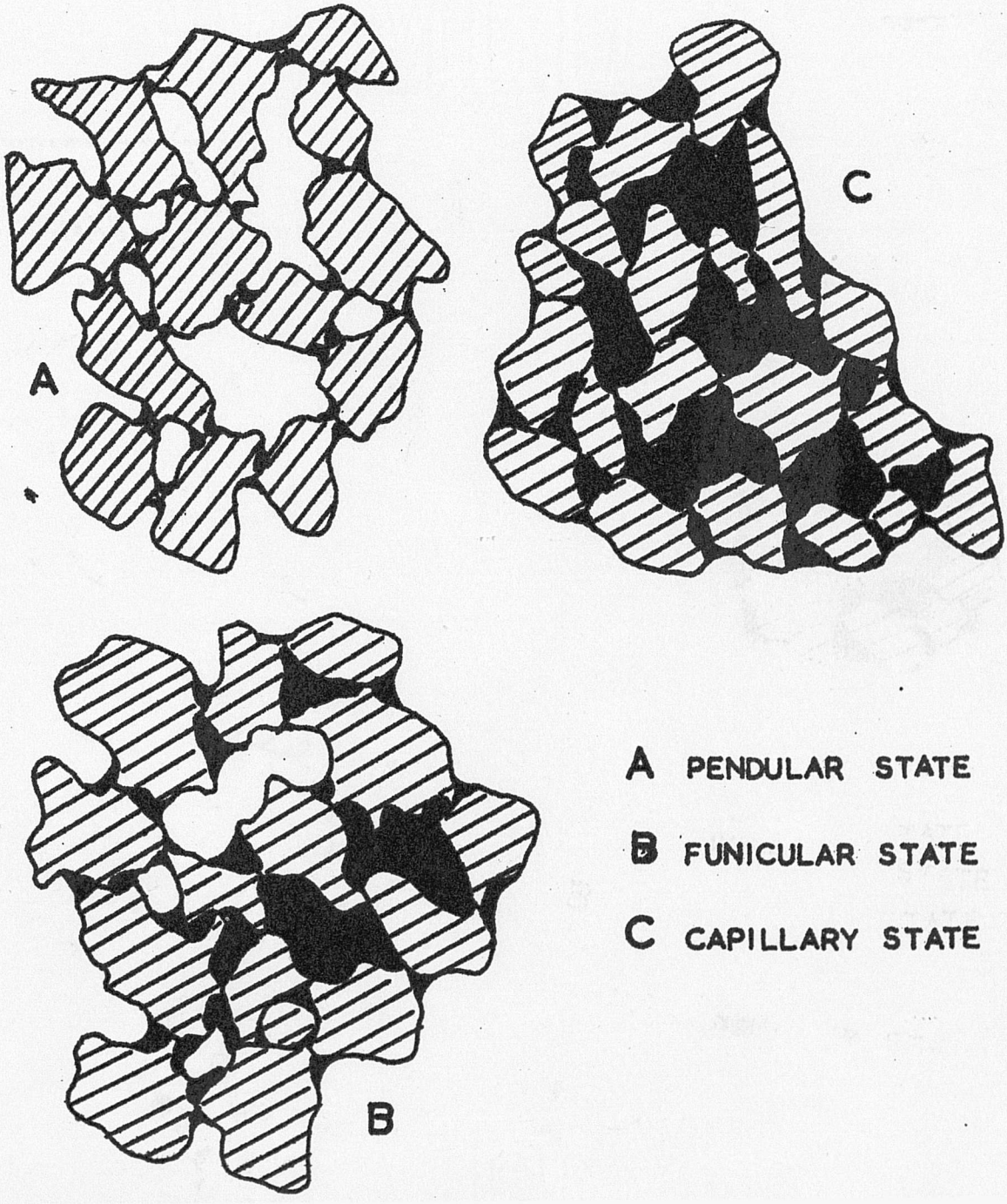
Donnan (29) was the first to put forward a theory of bonding forces in the agglomeration of fine particles. He held that the solubility of a homogeneous solid varied from one point of the solid particle to another, and generally the solubility was highest at the points which had been subjected to high stresses. The material could therefore dissolve at one point of the particle and was then reprecipitated at the points where the solubility was lower, resulting in the formation of crystalline bridges. The cementing action of these bridges was considered to be responsible for the strength of the "green" pellets, and was primarily of a chemical nature. Physical forces responsible for the process of agglomeration were not mentioned. The application of this theory to pellitizing

fine material had not been verified experimentally. The first important theories of pelletizing were those of Firth (30), and Tigerschoild and Ilmoni (31). In his investigations using iron ore, Firth observed that "the ease of balling" was proportional to the specific surface area of the material and that the green-strength of the pellets was the same as would be imparted by a briquetting pressure of several thousand p.s.i. This, he attributed to the compressive force exerted by the entire ball resting on a single particle. Tigerschoild and Ilmoni, however explained this phenomenon by a theory of green bonding through capillary forces due to the water in the voids of the pellets. The magnitude of these capillary forces was considered proportional to the pore diameter and to depend on the specific surface area of the material (32). This was in good agreement with Firth's (30) observations but the concept did not take into consideration the state where a pellet was only partially saturated with water.

Haines (33, 36) and Fisher (34) developed a theory of the bonding forces of water in a "capillary" state and in a "pendular" state. In a "capillary" state of saturation, all the voids in the pellet were considered to be filled with water while in a "pendular" state of saturation, the liquid in the voids was discontinuous and existed as discrete lenses at the points of contact of the particles only. (see Fig.2). Developing further from the concept they concluded that the strength of an agglomerate having a saturation in a

FIG 2

THREE STATES OF WATER CONTENT IN A PELLET



"capillary" state was 3 - 4 times that having a "pendular" state. Utilising the work of Haines (33) and Fisher (34), Newitt and Conway-Jones (35) derived an approximate equation for a "funicular" state in which the degree of saturation in the pellets was between that of the "capillary" state and the "pendular" state. (See Fig.2), resulting in the strength of the agglomerates intermediate between those corresponding to the other two states. Like Haines (36), they observed an increase in strength with increase in moisture content until a saturated state was reached, This is in good agreement with the observation by Cooke and Ban (37) of a similar strength - moisture content relationship, but conflicts with an earlier observation by Tigerschoild and Ilmoni (31) who found that the strength of green pellets could be increased by simultaneous rolling and drying.

The strength of green pellets depends, also, on other factors such as the packing properties of the particles, the nature of the liquid, etc. It is at least partly attributable to capillary forces; the influence of the surface tension of the liquid has, therefore, to be considered. Cooke and Ban (37) tried kerosene, a liquid of low surface-tension, for pelletizing iron ore and reported that the strength of the pellets was low. Ridgeon, Cohen and Lang (43) found an increase in the green strengh with sodium carbonate solution, which they attributed to the increase in surface tension of the liquid. The most conclusive experimental work on this aspect

was that of Newitt and Conway-Jones (35) who used water-alcohol solutions of varying concentration for pelletizing silica sand. The strength increased linearly with the surface tension of the liquid.

The mechanism of wet bonding can only be operative if the surface of the solid is hydrophilic. Smrceks, Rericha and Kandl (58) and Ban (25) experienced difficulties in pelletizing a normal flotation concentrate and they attributed this to the hydrophobic properties of the surfaces of the solid.

The green strength of the pellets should also depend on the chemical nature and viscosity of the liquid. If reaction occurs between the liquid and the solid to be pelletized, the surface tension as well as the viscosity of the liquid may change. The latter factor was investigated by Rumpf (50) who stated that the force required to disrupt a viscous binder was higher than that needed with a liquid of low viscosity. This was explained by the deformation energy of a viscous liquid being greater than the increase in surface energy of a mobile medium.

Depending on the material to be pelletized and the liquid used for the operation, the factors influencing the process of pelletizing vary from one system to another. Although Newitt and Conway-Jones (35) have described the mode of pellet formation of silica sand and have investigated the effect of particle size on pellet growth and pellet strength, the theory and practice of pelletizing fine powder is still difficult to generalize. Each

pelletizing problem has to be treated separately.

Work on the pelletizing of fine powders has been conducted by various workers, often on pilot-plant or production scale. The pelletizing of fertilizer was described by Hardesty and Chuka (38) and by Sherwin and Stevenson (50), while Swartzman (39) published an article on agglomeration in the coal industry using balling methods. Much attention has been directed to the pelletizing of iron ore. Pelletizing of magnetic taconite was investigated by Cooke and Ban (37), Cooke and Stowasser (40), Ban and Erk (41), Kunde (42) and many others, while Ridgeon, Cohen and Lang (43) pioneered the pelletizing of flaky haematite. Little has been published on pelletizing of other minerals. However, Cohen (44) successfully pelletized fine manganese dioxide concentrate in a pilot plant, and fly-ash from power stations is nowadays being pelletized on an industrial scale. The pelletizing of chromite has not previously been described and its specific problems were unknown. The hardness of the chromite, its shape factor, the size distribution of the particles, its refractoriness, the nature of the gangue material etc. make the pelletizing of chromite different from that of other materials. An attempt was therefore made to pelletize this material.

5.2 Pelletizing Apparatus.

A pelletizing apparatus consists essentially of a revolving vessel in which moist powder material can be formed into spherical agglomerates. Simple rotating drums or discs are commonly used although more complicated equipment has been proposed from time to time. Recently, Sterling (28) described a multiple cone pelletizer and claimed an advantageous longer retention time.

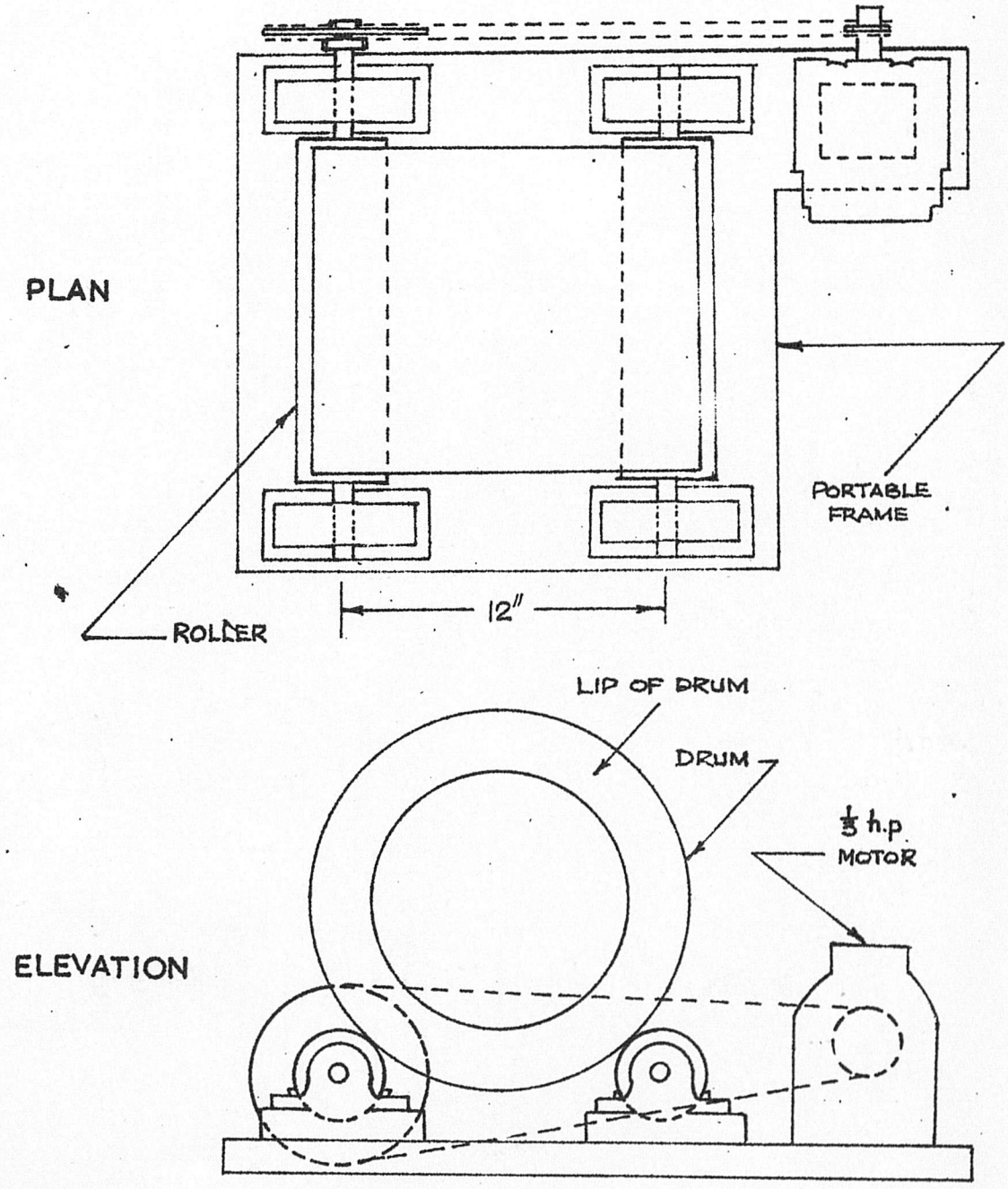
In this investigation three small laboratory drums were employed for batch pelletizing. They were 12", 14" and 17" in diameter and 12" long with smooth interior surfaces. One end of the drum was closed while the other end had a $2\frac{1}{2}$" lip for the retention of material in the drum.

In operation, a drum was supported by two $2\frac{1}{2}$" diameter rollers, horizontally spaced 12" apart, one of the rollers being driven by a $\frac{1}{3}$ h.p. a.c. motor through pulleys. The pulleys were changeable, providing a selection of speeds of rotation for the drum. This arrangement permitted easy interchange of drums of different diameters and facilitated cleaning (see Fig. 3).

In a batch pelletizing test, the ratio of pellets to powder at the beginning of the experiment is equivalent to the ratio of the circulating load to the feed-rate in a continuous process. This ratio is known as the equivalent circulating load which is normally expressed as percentage of the fresh feed; it tends towards infinity at the end of the test when no powder is

FIG 3

PELLETIZING APPARATUS



left in the load.

Consider a continuous pelletizing process using a drum pelletizer with one end receiving wet feed and returned seed pellets and the other end discharging pellets of various sizes. It may be taken that for a short period before pelletizing takes place, the extreme feed end of the drum has a load containing a proportion of seed pellets equivalent to the ratio of the circulating loadto the feed material. As pelletizing proceeds, this mixture of seeds and wet powder is displaced towards the discharge end of the drum while the powder is applied gradually to the seeds, thus forming bigger pellets. The ratio of pellets to wet powder therefore increases until no more powder is left in a section of the load. This is analogous to the pelletizing of a certain quantity of pre-formed seed pellets and wet powder as a batch in a laboratory drum. It is therefore possible to employ batch testing procedure to investigate a process which is normally continuous.

5.3. Quality Control of Pellets.

The green pellets must have adequate resistance to abrasion, compression and impact to survive different stages of handling prior to hardening at high temperatures,

Various test methods for determining the strength of pellets have been used. Resistance to breakage tests by controlled dropping were employed by Tigerschoild and Ilmoni (31) and by Urich

and Han (45). The method was further modified by Ban and Erk (41) who introduced the concept of strength index, defined as the ratio of the average size of the material after impact to the average size of the material before impact. This index, however, seems to give little indication of the resistance of pellets to impacts received during actual handling. The number and height of falls during conveyance vary from plant to plant. The disposition and nature of the surface on which pellets fall are further factors of importance, greater heights of fall being acceptable on to a bed of pellets than on to an unyielding metal or concrete surface. The dropping of pellets on to a steel plate may hence be regarded as an unrealistic measure of their strength. Ridgeon, Cohen and Lang (43) found that for drops of greater than 2 - 3 feet all the haematite pellets broke the first time; and from less than 2 - 3 inches, the pellets never broke. At intermediate heights almost all broke at the second drop.

Tumbling tests have been used to determine the pellets' resistance to abrasion. They produce mutual rubbing between pellets in a small rotating drum for a predetermined period. The quantity of fines produced is taken as an inverse measure of abrasion resistance. This method was used by Ban and Erk (41), Tigerschoild and Ilmoni (31), Urich and Han (45) and others in testing fired or dried pellets. Depending on the quality of the pellets and rolling period, up to 20% - 28 mesh material could be

produced through this tumbling action (45). This method of testing, however, does not apply to pellets which tend to pick up any fines produced by abrasion in a tumbling tester, and, in the case of fired or dried pellets, the significance of this test method is dubious unless it can be designed to simulate actual specific working conditions.

By far the most commonly accepted method of determining the quality of pellets is the compression or crushing test. This involves placing a pellet between two flat plates of steel and applying an increasing uniaxial load until failure of the specimen is observed. The breaking load is taken as the compressive strength of the pellet. The main defects of this method lie in the difficulty of applying the load at a constant rate and in the indeterminate size of the areas on contact between the pellet and the compressing plates.

Under normal operational conditions, pellets are frequently subjected to a multiaxial compression by adjacent pellets and this can be simulated by compression testing of a pile of pellets but the result indicates mainly the multiaxial compressive strength of the weakest pellets in the batch. The average strength of the pellets is not determined.

None of the above methods of testing is completely satisfactory; nor does any simulate adequately actual operational environments. However, owing to the simplicity of operation,

compression testing of single pellets was adopted in this work.

This method is well documented. Ban and Erk (41), also Tigerschoild and Ilmoni (31) stressed the importance of the rate of application of the crushing load and careful experimental techniques are necessary for obtaining reproducible results. Newitt, Wood and Hansen (46) applied their crushing load by adding drops of mercury into a container resting above the pellet. A more elaborate method was devised by Stevenson and Bergstrom (47) whereby the deformation of the pellet could be measured with increasing compressive load. However, in most cases, manual application of load was found to be sufficiently reproducible to be employed for rapid determinations.

In this investigation, a manually operated Salter Compression Tester with an interchangeable scale was used for determining the compressive strength of the green pellets. With this set-up it was possible to determine compressive strengths from a fraction of a lb. to 44 lbs. The compressive strength of the fired pellets was determined with a Millen Mounting Press. Compressive strengths of over 2000 lbs. could be determined. Reproducible average results were obtained by testing 10 to 20 pellets from each batch.

5.4 Strength-Size Relation of Pellets.

The ability of a pellet to withstand a compressive load depends on its diameter when other parameters are constant. This was first enunciated by Tigerschoild and Ilmoni (31) who stated that the compressive strength of a pellet should be proportional to the square of the diameter. Newitt and Conway-Jones (35) found a similar relation with silica sand pellets and, according to Tigerschoild (48), Ilmoni and Uggla produced the same conclusion with iron-ore pellets.

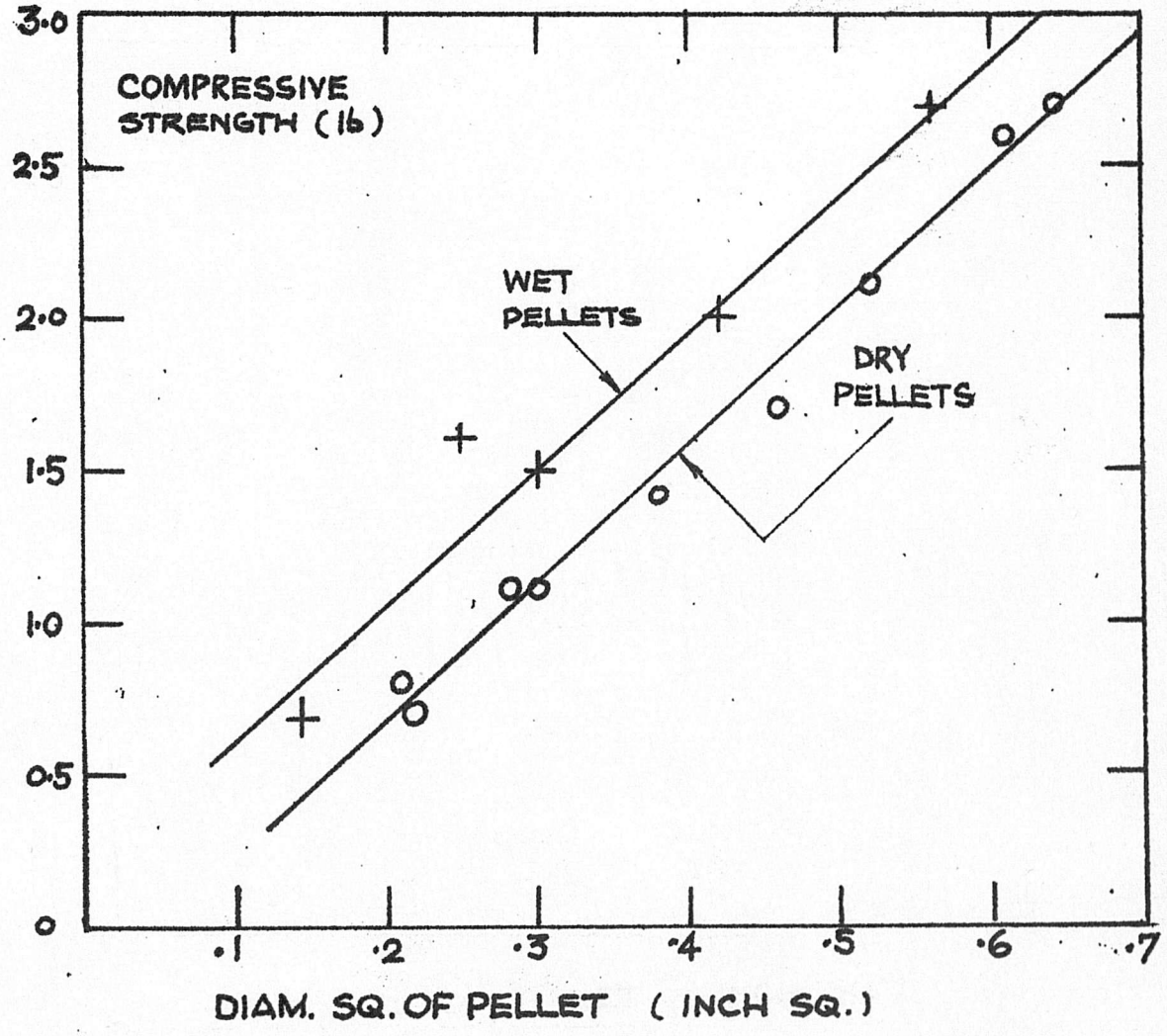
In order to investigate the strength-size relationship of chromite pellets compression tests were carried out on batches of pellets of different sizes. The compressive strength was found to be directly proportional to the square of the average diameter of the pellets and this relationship held for pellets made from dry feed as well as those made from wet material, as shown in Fig. 4.

As usual in sampling, it was impossible to obtain samples of pellets of exactly uniform size. For the purpose of comparing pellets of different sizes, a correction had to be applied to the measured values of compressive strength. In all cases the values were corrected to a standard pellet of 0.6 inch diameter, allowing the compressive strengths of different batches to be compared.

The correction required exact measurements of the diameter of the pellets. This could be measured readily by means of a small ruler. If a pellet was found to be non-spherical, the

FIG 4

STRENGTH-SIZE RELATION OF PELLETS



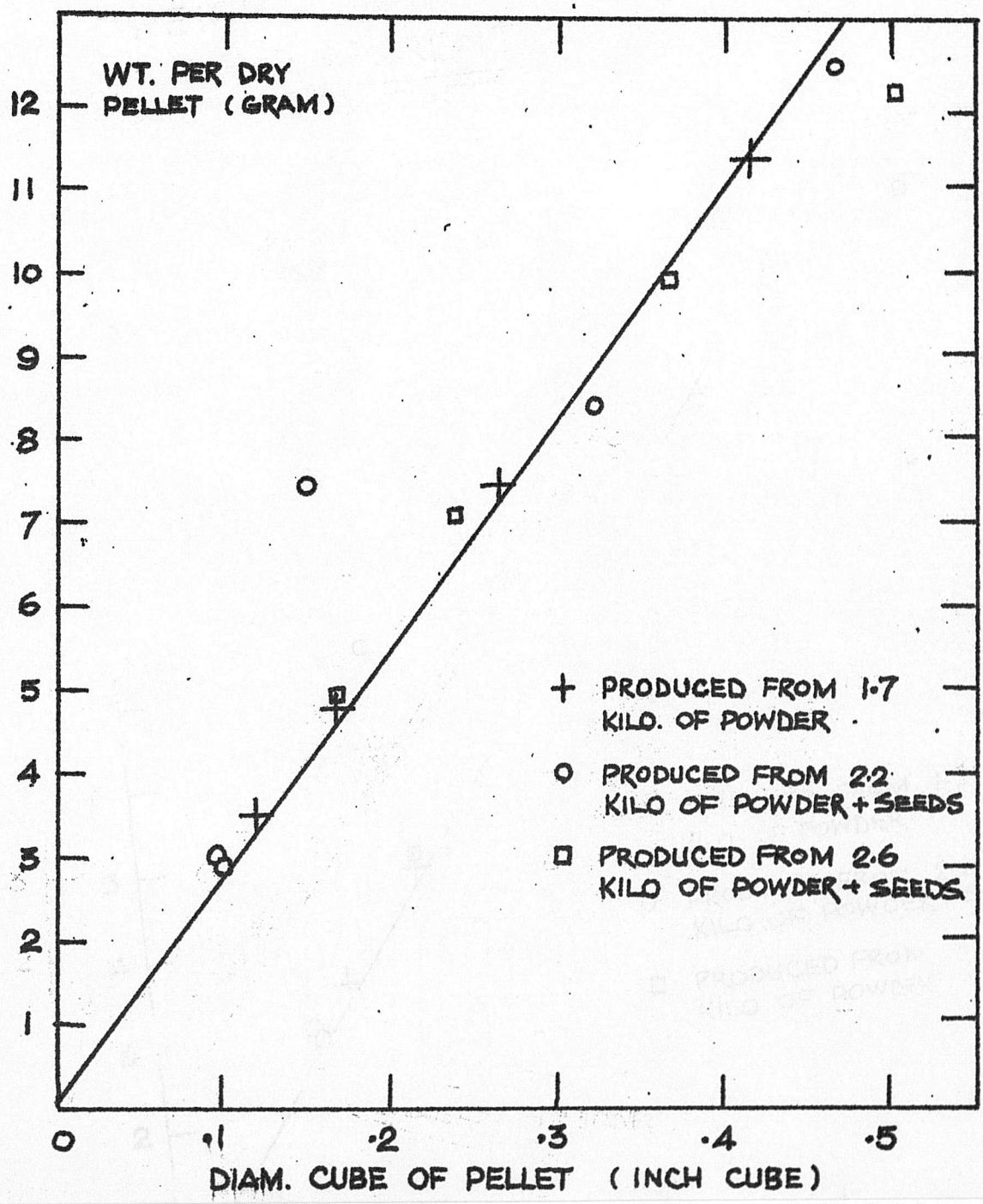
diameter of the equivalent sphere was determined from its weight. This was possible because the apparent density of the pellets was found to be independent of size and consequently their weights were directly proportional to their volumes (see Fig.5).

5.5. Pelletizing Dry Powder Without Seeds.

In studying the mechanism of pelletizing, it was desirable to observe the onset of the process of pellet formation. Early trials of pelletizing chromite concentrates were, therefore, conducted with dry materials but without seed pellets.

The investigations were carried out in the 14" pelletizing drum rotating at 34 r.p.m., with an equivalent peripheral velocity of 125^{1}/min. At this drum-speed it was observed that the powder did not tumble but slid up and down the wall of the drum with an oscillating motion as one mass. Water addition in the form of a fine spray created an almost uniform layer of wet material at the surface of the load. All the wet particles adhered to one another by surface tensional forces to form one continuous layer, which behaved like an elastic skin covering the rest of the dry material. There was no tendency for the wet material to break away from the load, and there was no mixing between the wet surface layer and the dry powder beneath. Pellet formation did not occur and further addition of water by fine sprays could only increase the thickness of the layer of wet material, until the whole load became too wet

FIG 5
WEIGHT–VOLUME RELATION OF DIFFERENT PELLETS



to be pelletized.

A less dispersed small jet was used as an alternative method of water addition. The larger droplets of water created randomly spaced granules consisting of loosely packed wet particles adhering to one another. Their voids were completely filled with water and according to the capillary theory of pelletizing (31) the surface tensional forces tended to pull all the wetted particles at the surface towards the centre of the granule, forming a denser structure. On rotating the drum, these small granules broke away from the rest of the load or sank further into the mobile powder. These granules were then subjected to rolling and compaction, squeezing surplus water to their surfaces and enabling them to pick up the remaining surrounding dry material. In this manner the granules rapidly grew into small seed pellets which mixed well with the remaining powder. The growth of seed pellets would continue on receiving more water, but owing to the high ratio of powder to seeds at the beginning of the process, it was found difficult to direct the water entirely on the seed pellets. Any water addition tended to wet the powder to a much greater extent than the seeds, resulting in formation of further seeds and only slow growth to larger pellets. The size of pellets formed in this manner was irregular and depended to a great extent on the initial load of dry material in the drum. It was found that with a fixed, short period of water addition, mainly small pellets were

produced from a small load and bigger pellets were obtained as the load was increased. This continued until the dry load in the drum was in the region of 2 kilograms. Further increase in the load in the drum again resulted in an excessive formation of small pellets. The amount of large pellets was also reduced (see Table 5)

TABLE 5.

Effect of Load on Size of Finished Pellets in the Absence of Seed Pellets

		Size Distribution of Finished Pellets (%)		
Run	Dry Load in drum (g)	$+\frac{3}{4}$"	$-\frac{3}{4}$" $+\frac{1}{2}$"	$-\frac{1}{2}$"
1	500	-	16	84
2	900	-	55	45
3	1100	34	59	7
4	1300	40	56	4
5	1600	76	20	4
6	2200	69	31	-
7	2600	53	45	2
8	3000	32	57	11

Size of Drum 14"

Speed of Drum 125^{1}/min (34 r.p.m.)

In the course of the pelletizing trials, it was observed that pellets appeared first as loosely packed, small granules which picked up more dry material as the pelletizing process proceeded. With a small load, most of the dry material was rapidly converted into small seed pellets and there was

little material left for pellet growth. With larger loads in the drum, the size of the pellets tended to increase not only through pick-up of fine material, but also through coalescence of aggregates and collecting of small granules by larger pellets (see Fig.6). The latter mechanism resulted in rapid pellet growth at the expense of the small granules, and, although a range of pellet sizes still existed, the proportion of small pellets was markedly reduced, as shown by runs 5 and 6 in Table 5.

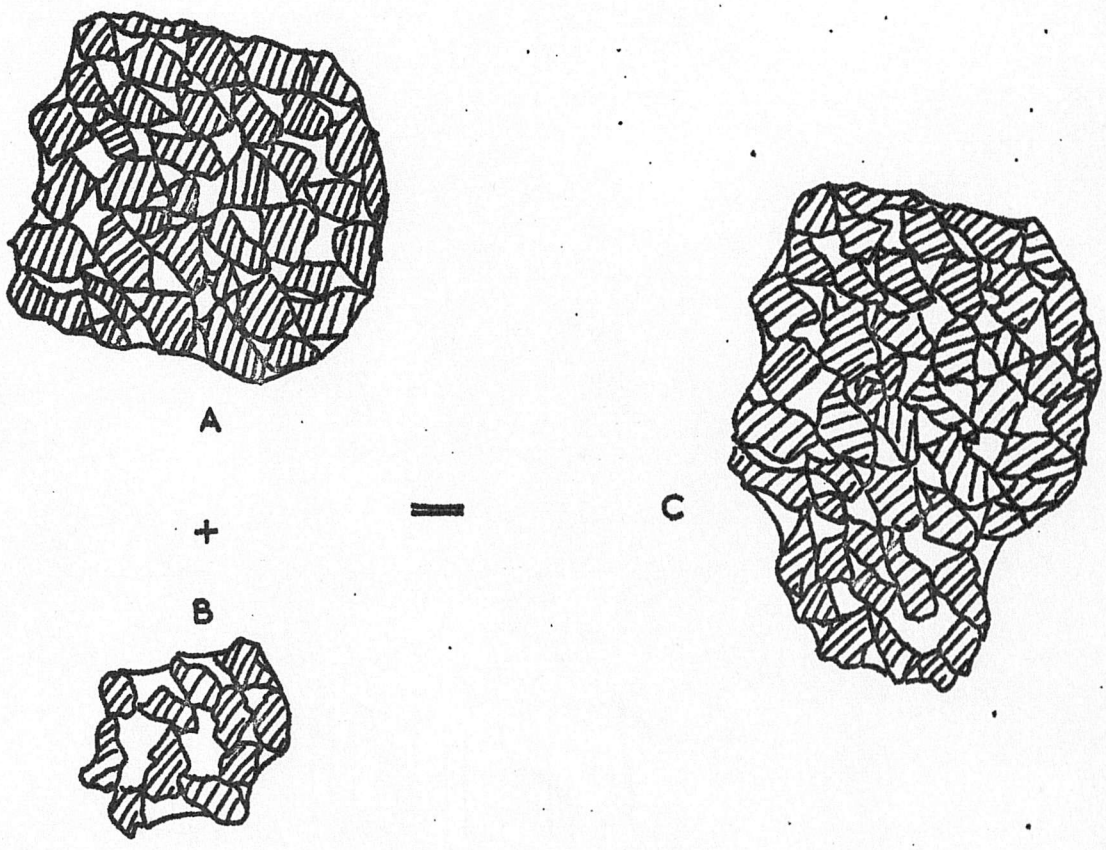
On increasing the load in the drum further, a stage was reached when the rolling action was increasingly replaced by cascading and irregular tumbling motion of the bed. Intimacy of contact decreased, and pellet growth slowed down. The powder, thus, had more opportunity to receive water from the sprays, causing increased formation of seeds. This resulted in excessive seed pellets and insufficient fully formed product. The optimum load for a batch-drum of this size was found to be about 2.0 kilograms of dry material as indicated in Table 5. This was equivalent to approximately 1.7 kilogram per foot diam. per foot length of drum.

5.6 Pelletizing Dry Powder With Seeds.

In view of the importance of seeding in the process of pellet formation, pelletizing of dry chromite concentrate with seed pellets was investigated. -½" seeds were prepared by

FIG 6

ILLUSTRATION OF GROWTH OF SEED PELLETS



A = SEED — CLOSE PACKED

B = 'WET' GRANULE — LOOSE PACKED

C = GROWTH OF 'A' BY COALESCING WITH 'B'

rolling batches of 900 grams of dry material in the 14" drum as described in the previous section. When a sufficient amount of seeds had been collected, they were pelletized with dry powder.

It was found that the powder in the drum could not be considered completely dry. During the addition of water to the load, it was found difficult to direct the water solely on the seeds. There was intimate mixing between the seeds and the powder and addition of water caused wetting of seeds and powder to occur simultaneously. In effect, the seeds were picking up wet powder with an unknown moisture content. In addition, wet agglomerates of irregular sizes were also produced by the removal of excessive accumulations from the wall. Pelletizing by means of moisture addition to a dry feed thus lacked quantitative control and depended largely on the skill and judgement of the operator. It was therefore considered more realistic to pelletize a moist feed with a known moisture content.

5.7 Pelletizing Wet Powder Without Seeds.

A desired moisture content of the feed material could be obtained by wetting samples of dry powder with an excess of water and then removing the surplus moisture by filtering in a Buchner funnel. By careful adjustment of the drying time during filtration, a controllable moisture content could be easily obtained in the filter cake. This was rapidly disaggregated to

$-\frac{1}{8}$" and was then used as wet feed to the drum. This method of sample preparation produced a feed material with a uniform moisture content. This would be difficult to achieve if a measured amount of water was added to a dry sample without an elaborate set-up for mixing.

Samples of disaggregated wet material with a moisture content from 7.5 to 12.5% failed to form pellets in the drum without agitation or further addition of water. Loosely packed aggregates of wet material formed and showed a tendency to coalesce to one coherent mass, sliding in the drum. Changes in the load, drum diameter, or peripheral velocity could only transform the sliding motion of the load into a tumbling action, breaking large aggregates into smaller ones, but did not result in pellet formation. Further addition of water created a spongy mass of wet material in the drum. No balling was seen to occur.

Slight agitation of the load, for example, by introducing a few $\frac{1}{2}$" pellets, caused very small ($-\frac{1}{4}$") seed pellets to appear after a comparatively long rolling period of the order of 5 mins. No further growth of these seeds was observed.

However, if wet, larger and more densely packed aggregates accidentally occurred in the feed, they tended to break away from the rest of the wet material, roll readily in the drum and pick up more wet feed, thus forming large pellets. It was, therefore, apparent that the formation of pellets from a wet feed

also necessitated "seeding" of the material with small well-formed aggregates of wet material. This could be induced either by incomplete disaggregation of filter cakes, by using excessively wet feeds or by pre-forming devices such as extrusion. The quantity and size of seeds could not be adequately controlled and the pelletizing process resulted in pellets of highly irregular sizes in the finished product. Controllable formation of pellets would require the maintenance of a steady circulating load of seed pellets in proportions depending on other rolling variables such as feed rate to the drum, diameter of the drum, speed of rotation, moisture content of the feed etc.

5.8 Pelletizing Wet Powder With Seeds.

Preliminary examination showed that a feed containing 7.5 to 12.5% moisture could coat seed pellets without further addition of water. The average diameter of the seed pellets produced after pelletizing was approximately the same as that of the seeds added initially; this was in the order of 0.3 inches. With the above moisture content in the feed, pellets formed rapidly, in about one minute, provided that the amount of seeds was in excess of 100% of the feed. In view of this nearly constant period of pelletizing, the initial amount of powder in the drum could be regarded approximately as the equivalent feed-rate in gram. per minute. The rapidity of pellet formation also enabled

water addition to be discarded, eliminating a variable in the process.

Pelletizing:

In this investigation, a mixture of seeds (9.8% H_2O) and powder (10.0% H_2O) was added to the drum and pelletized for two minutes. The first minute was intended for pellet formation and pellet growth and the second minute for final rolling and compaction to impart greater strength to the pellet. The load was then removed and the amount of $-\frac{1}{2}$" pellets produced determined.

An increase in the amount of $-\frac{1}{2}$" seed pellets after pelletizing indicated an increasing circulating load in a continuous process. On the contrary, if the amount of $-\frac{1}{2}$" pellets had decreased, the circulating load of a continuous process would have diminished. Consequently, a stable circulating load was indicated by a production of $-\frac{1}{2}$" pellets equal to the quantity initially added to the batch-drum.

Feed-Rate:

The effect of the feed-rate on the stability of the circulating load was investigated by means of batch testing with different equivalent feed-rates and different equivalent circulating loads, in different sizes of drums. The results are shown in Figs. 7, 8 and 9.

The amount of $-\frac{1}{2}$" seed pellets produced in each batch depended on the initial ratio of seed pellets to powder, and on

FIG 7

EFFECT OF WET FEED ON CIRCULATING LOAD

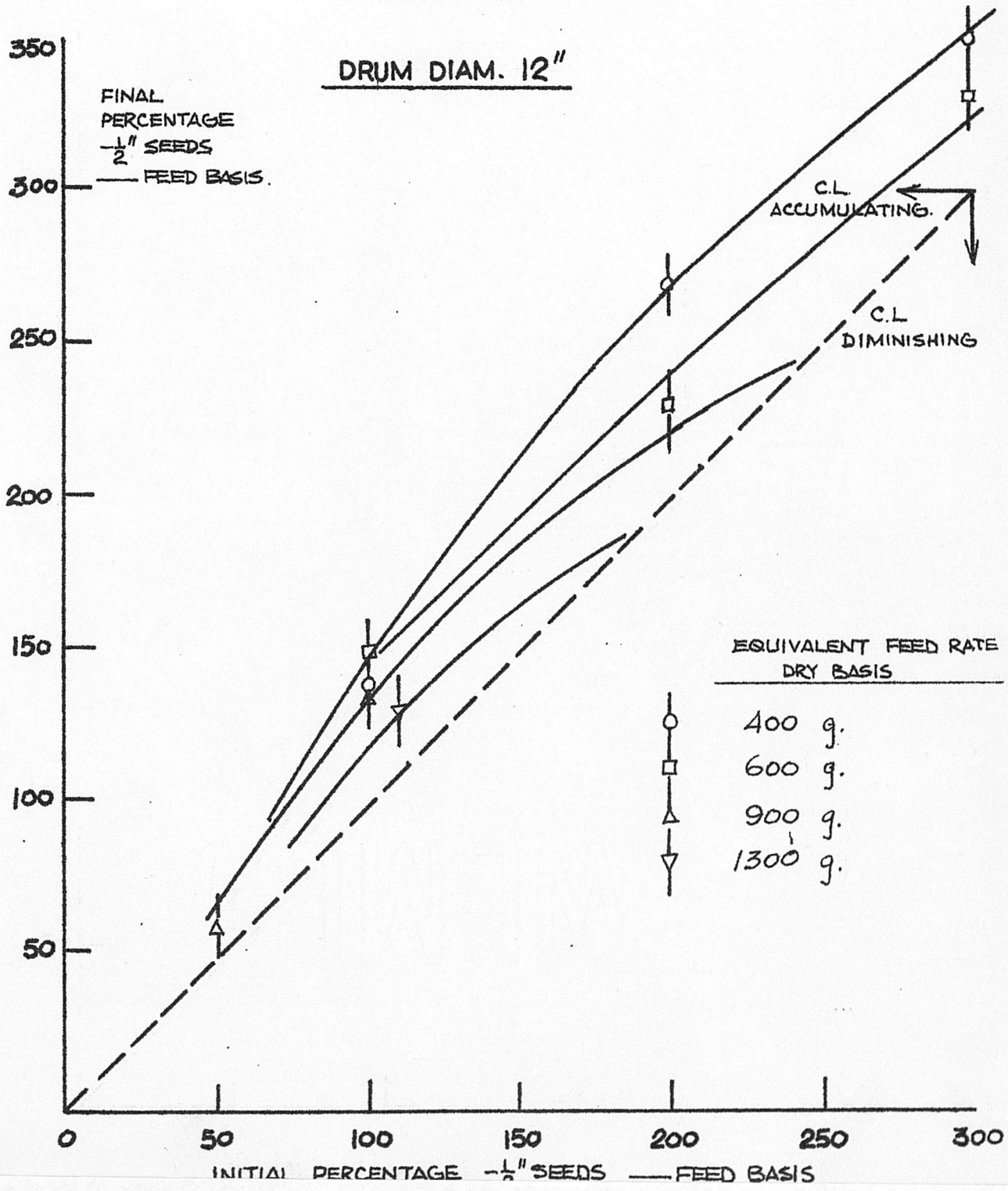


FIG 8

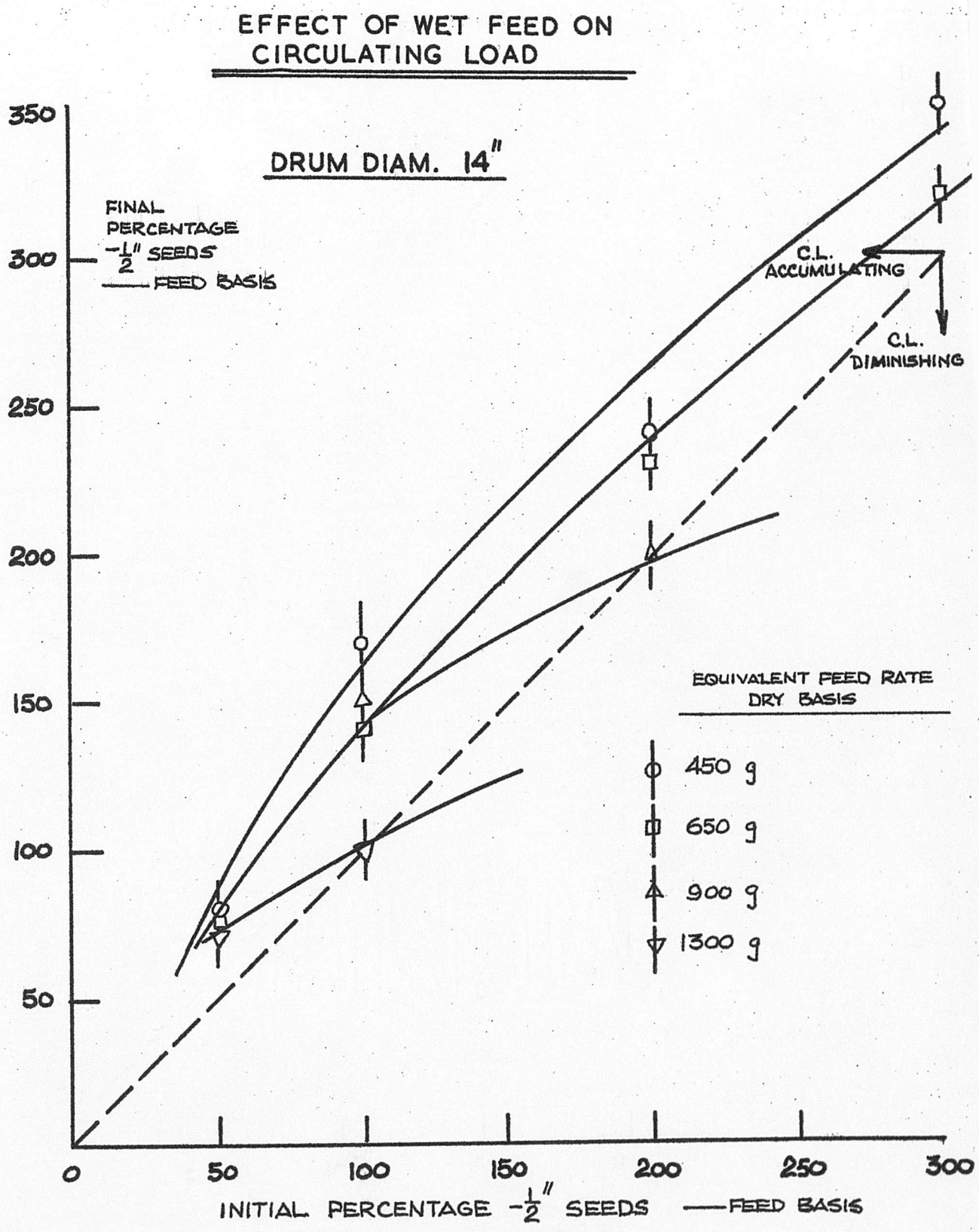
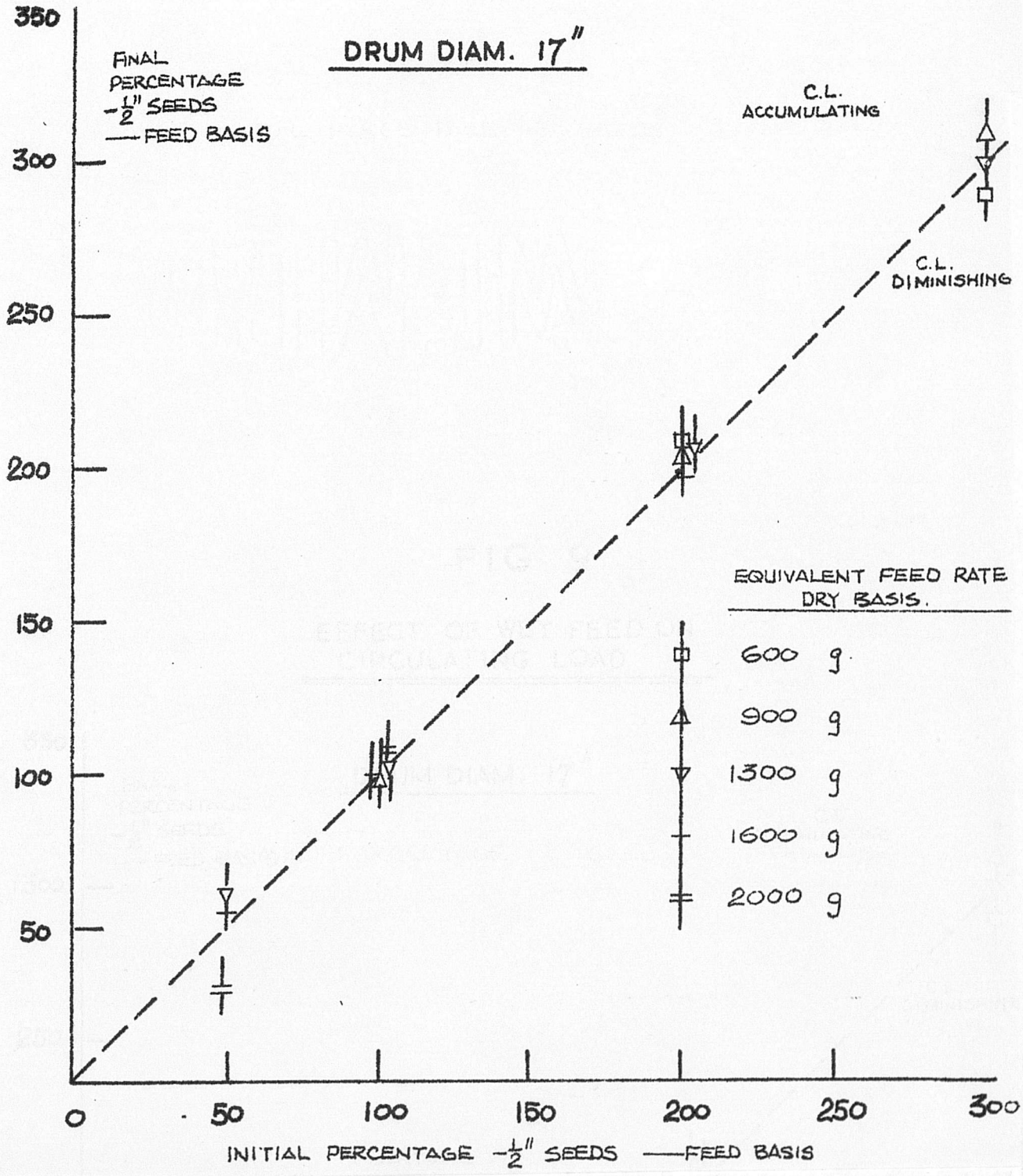

EFFECT OF WET FEED ON CIRCULATING LOAD
DRUM DIAM. 14"
FINAL PERCENTAGE -½" SEEDS —— FEED BASIS
C.L. ACCUMULATING
C.L. DIMINISHING
EQUIVALENT FEED RATE DRY BASIS
450 g
650 g
900 g
1300 g
350
300
250
200
150
100
50
0
50
100
150
200
250
300
INITIAL PERCENTAGE -½" SEEDS —— FEED BASIS

FIG 9

EFFECT OF WET FEED ON CIRCULATING LOAD



the initial amount of powder in the load. For a given equivalent feed-rate in a given drum, there appeared to be a corresponding equivalent circulating load. In a drum rotating at a constant velocity, a high equivalent feed-rate gave a low equivalent stable circulating load and conversely, a low equivalent feed-rate resulted a high equivalent circulating load. In practice, the rate of feed and the circulating load can fluctuate independently or simultaneously. If the circulating load momentarily falls below or rises above the stable circulating load, the amount of seed pellets will gradually accumulate or diminish accordingly until a stable circulating load is again reached. A sudden fluctuation in the feed rate will also result in a temporary lower or higher percentage circulating load. If the percentage circulating load is lowered i.e. by an increasing feed rate, the amount of seed pellets will adjust itself until a new equilibrium is reached. On the contrary, if the percentage circulating load is raised i.e. by a decreasing feed rate, the amount of seed pellets will be altered to another equilibrium condition so that the new circulating load corresponds to the new feed rate. This process is self-adjusting and can tolerate limited fluctuations, if adequate arrangements can be made to handle the surge of seed pellets.

During the investigation, it was also observed that little mixing between the seeds and the powder occurred when the total load in the drum was small. In a 14" drum insufficient

mixing was found in a load of less than 0.5 kilogram of mixture. After prolonged rolling, however, numerous very small pellets having a diameter of the order of $\frac{1}{8}$" appeared but they failed to grow in size. It seemed that the formation of excessive seed pellets was mainly due to the rolling of wet material without sufficient agitation, and the failure of growth of seed pellets was attributed to inadequate contact between the seeds and the powder owing to poor mixing. When the total load was increased, more thorough mixing occurred and pellet growth became rapid. The seed pellets coalesced with wet, loosely packed granules, forming bigger pellets with a loosely packed surface layer. These pellets worked their way to the toe of the charge and compacted there through rolling on the harder drum layer. As pelletizing proceeded, these pellets were again submerged in the remaining unagglomerated powder where they acquired yet another layer of material on their surfaces. A layered structure of the pellets was thus resulted. Pelletizing generally proceeded satisfactorily if adequate collision between the seeds and the wet powder was achieved. Proper mixing of the load during pelletizing was therefore essential.

Interpreting the results of batch-pelletizing in terms of a continuous production process, the following sequence of events is envisaged: A small feed-rate to a drum requires a larger amount of seed pellets to make up a large total load

facilitating mixing and, therefore, pellet formation. If insufficient seed pellets are present, the total load in the drum is less and the rate of pellet growth will be slow. This causes a build-up of seed pellets resulting in a high circulating load for a low feed-rate. On the contrary, a large feed-rate only requires a small circulating load to make up the required total load in the drum. The stable circulating load for a high-feed rate is hence lowered. Further increase in the circulating load while the feed-rate is still high, gives rapid building-up of pellets owing to the increase in surface area of the seeds. Little powder material is left for the formation of new seed pellets and the circulating load, therefore, diminishes.

5.9 Effect of Moisture Content of Seeds and Feed on Pelletizing.

Loading of the drum is, however, not the only requirement of good pellet formation. The moisture content of the feed and the seed pellets are also important factors.

Newitt and Conway-Jones (35) reported that pellet formation was rapid with a high moisture content in the feed and slow if the moisture content was decreased. Pelletizing of chromite concentrate was found possible with a feed moisture content of 7.5 to 12.5% by weight, but its effect on the circulating load remained to be investigated. This applied also to the moisture content of the seeds.

A procedure similar to that used in previous investi-

gations was adopted in this series of tests, in which the seeds and the powder were pelletized in the 14" drum for two minutes. The adjustment of moisture content in the feed was regulated through the drying time during filtration, while the moisture content in the seeds was altered by rolling them in a drum. The results are shown in Tables 6 and 7.

TABLE 6

Effect of Moisture Content in Feed on Pelletizing

	Percentage water in feed	Percentage Circulating Load	
		Initial	Final
A.	15.0	100	140
	12.5	100	130
	10.0	100	110
	8.7	100	150
B.	10.4	200	200
	10.0	200	210
	9.5	200	230

Moisture Content in Seeds 9.8%

Equivalent Feed-Rate A - 1.3 kilo/min (dry basis)

B - 0.9 kilo/min (dry basis)

TABLE 7

Effect of Moisture Content in Seed Pellets on Pelletizing

Percentage Water in Seeds	Percentate Circulating Load	
	Initial	Final
10.5	100	150
9.6	100	110
9.1	100	110
9.0	100	100

Equivalent Feed-Rate 1.3 kilo/min (dry basis)

Moisture Content in Feed 10%

It has been shown in section 5.8 Fig. 8 that a 100% circulating load could be maintained by a feed-rate of 1.3 kilogram per minute and a 200% circulating load by a lower feed-rate of 0.9 kilogram per minute, with a feed moisture content of 10% and a seed moisture content of 9.8%. However, the present tests showed that if the moisture content of the feed was increased to over 10% rapid formation of $-\frac{1}{2}$" wet lumps of irregular sizes occurred resulting in a rising circulating load. If the moisture content in the feed was reduced to below that of the seeds i.e. -9.8% the circulating load was again found to increase (see Table 6).

It was noted that the feed showed a certain tendency to form loosely textured granules, even after disaggregation.

This tendency was observed to increase with increasing moisture content. The existence of a large amount of such wet granules in the feed, capable of turning rapidly into seed pellets was believed to be responsible for the increase in seed pellets with excessively wet feeds. In a feed with low moisture content, very few wet granules existed and hence, growth of seeds proceeded slowly by acquisition of a few grains at a time. The incremental material was held to the surface of the seeds by pendular bonds. Owing to such slow growth, sufficient time was available for the formation of additional nuclei in the wet material, resulting in excess proportions of $-\frac{1}{2}$" pellets. In addition, abrasion of the comparatively dry pellets during rolling contributed to a decrease in $+\frac{1}{2}$" pellets. On raising the moisture content of the feed the amount of small, loosely packed granules increased. Growth of seed pellets by coalescing with these granules was rapid and resulted in a large amount of $+\frac{1}{2}$" pellets and a small proportion of seeds. This stage was achieved with a feed moisture content of the order of 10.5%.

Table 7 shows the effect of moisture content of the seeds on the circulating load, with the moisture content of the feed kept at 10%. Provided sufficient granules were present in the seed, a low moisture content in the seeds did not affect the circulating load of the process. On raising the moisture content in the seeds to excess, irregular accretions appeared on the wall

of the drum. Dislodging of this accumulation led to the formation of seeds and rapid increase in the circulating load.

The optimum moisture content for pelletizing this material was 10.0 to 10.5% for the feed and 9 to 10% for the seeds.

In practice the moisture content of the seeds cannot exceed that of the feed without further water addition. Hence if the moisture content of the feed is carefully regulated, a stable circulating load can be obtaind.

5.10 Effect of Drum Diameter on Circulating Load in Pelletizing.

The diameter of the drum was expected to have an influence on the growth of pellets which depends on the collision between seeds and wet materials. The effect of drum diameter on the circulating load was, therefore, investigated.

This was conducted by pelletizing a predetermined amount of wet feed and seed pellets in a 14" pelletizing drum for two minutes after which, the product was removed from the drum and screened for the determination of the amount of seed pellets in the load. An increase in the amount of seed pellets denoted an increase in the circulating load and a decrease in the amount of seed pellets denoted the opposite effect. In order to examine the effect of drum diameter on the circulating load all the three laboratory pelletizing drums were used. They were of 12", 14" and 17" internal diameter.

It was found that the 17"drum was not only capable of handling a high feed-rate but could also operate at low feed-rates without raising the stable circulating load appreciably. A smaller drum worked well with a comparatively high feed-rate and with a high circulating load only (see Table 8). Consequently, fluctuation in the circulating load caused by changes in the feed-rate should be more apparent in a small drum than in a bigger one. This was confirmed by tests, the results of which are shown in Figs. 7, 8 and 9. It can be seen that changes in the feed-rate did not alter the stable circulating load in the 17" drum, whereas any changes in the feed-rate in a small drum affected the stable circulating load.

TABLE 8

Feed-Rate of Wet Material to Drum for the Maintainance of a Stable Pre-determined Circulating Load

(Feed-rate of wet material in g/min - dry basis)

Percentage Circulating Load	50	100	200	300
Drum diameter : 14"	800	650	450	350
Drum diameter : 17"	650-1000	450-1000	300-300	200-650

Speed of rotation ~~34 r.p.m. or~~ 125'/min.

The difference is thought to be due to the greater curvature of the wall of a small drum disposing the load at a steeper angle during pelletizing. A small load readily causes segregation of the seeds from the powder while a larger load leads

to cascading, both creating excessive rates of seed formation. With large drums having walls of lesser curvature, segregation of seeds from the powder does not take place even at a comparatively small load, and cascading arises less readily. A large drum is, therefore, preferable to a small one in respect of throughput and flexibility.

5.11 Effect of Peripheral Velocity on Circulating Load in Pelletizing.

The growth of pellets was expected to be affected by the peripheral velocity of the drum. Previous investigations (ref. section 5.8) showed that a stable circulating load of 100% could be maintained by an equivalent feed-rate of 1.3 kilogram/minute in a 14" drum rotating at a peripheral velocity of 125'/min (34 r.p.m.). A change in this velocity led to an increase in the circulating load as shown in Table 9.

TABLE 9

Effect of Peripheral Velocity on Percentage Circulating Load During Pelletizing

angular velocity peripheral velocity	20 rpm 75 '/min	27 rpm 100 '/min	34 rpm 125 '/min	41 rpm 150 '/min
initial circulating load	100%	100%	100%	100%
final circulating load	160%	140%	110%	120%

Moisture content of feed 10.0%

Moisture content of seeds 9.8%

At lower peripheral velocities (under 125'/min), little mixing between the seeds and the wet material occurred and the frequency of collision decreased. This resulted in slow pellet growth and rapid formation of seeds. At velocities over 125'/min, thorough mixing took place, but the load was carried too high up the wall of the drum, causing cascading. The pellets rubbed against one another and against the wall of the drum. The pellet size was reduced by this abrasive action. This resulted in a slow rate of pellet growth and facilitated the rapid formation of new seeds from the fines produced. A peripheral velocity of about 125'/min. appeared to be the optimum for efficient pelletizing with the material and apparatus used in this investigation.

5.12 Bonding Mechanisms in Green Pellets.

The resistance of a pellet to deformation and breakage is attributed to bonding forces which may be grouped under the following headings.

1. Surface tension effect.
2. Physical interlocking.
3. Cementation by binding agents.
4. Forces of the physico-chemical nature.

Surface tension effect.

The effect of surface tension forces on the strength of a wet pellet depends on the magnitude of the surface tension

of the liquid, the state of saturation of the voids of the pellet and the wetability of the surfaces by the liquid.

In the case of a pellet consisting of particles with hydrophilic surfaces and with all the voids filled with liquid surface tension forces can only exist at the surface of the pellet in areas with concave meniscus facing the gas phase. In accordance with the capillary theory, a negative pressure will then exist in the entire liquid phase inside the pellet, providing it with a certain tensile strength. Thus, the pressure exerted by a liquid of surface tension γ in a capillary of radius r where the angle of contact is θ, is given by $2(\gamma/r) \cos \theta$. This state of saturation was considered by Newitt and Conway-Jones (35) who reported a tensile strength of a magnitude of 1 to 3 lb./sq.in.

This state of saturation is rarely attained in a pellet. During pellet formation, air is trapped inside the pellet and the state of saturation is more likely to be that of a "funicular" state (ref. Fig.2), which is normally regarded as a continuous network of water interspersed with air. At a lower moisture content, the water in the pellet will be further dispersed by air. It will centre round the points of contact of the particles in lens-shaped rings assuming a "pendular" state.

When a pellet is compressed it will deform before breakage eventually occurs. This deformation causes an increase in volume in accordance with Reynold's principle of dilatancy (49),

and the voids, therefore, become less saturated. In practice it may be seen that the surface of a pellet appears drier on slight deformation by compression, although its average moisture content remains unchanged. The saturation of the voids of a pellet can be regarded as having decreased and pendular bonds can, thereby, be formed. Further compression leads eventually to breakage, with the plane of fracture passing through the weakest points of contact (i.e. the weakest pendular bonds). The strength of a pellet due to the presence of liquid in the voids, can be regarded as dependant on the strength of the pendular bonds.

The surface tension forces involved in a pendular bond holding two spherical particles together has been expressed by the equation (35)

$$F = \frac{2\pi r T}{1 + \tan \frac{1}{2}\theta}$$

where F = pressure at point of contact

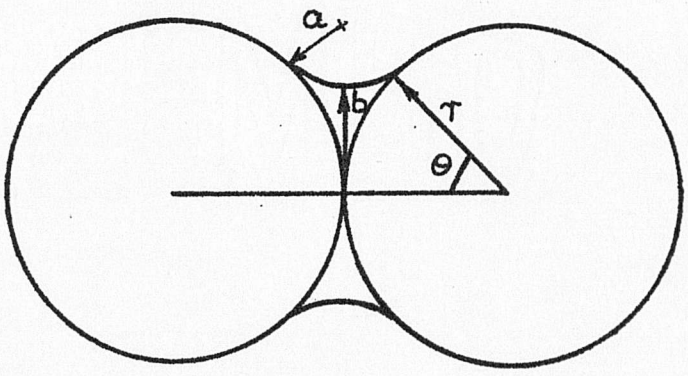
T = surface tension of liquid

θ = semi angle subtended by the meniscus (see Fig.10)

The equation shows that F increases with decreasing value of θ, i.e. the pellet strength increases with decreasing moisture content. This theoretical treatment applies only to spherical particles. For other particle shapes and configurations a decrease in the radius of the ring of pendular water is not necessarily compensated by a corresponding increase in curvature of the

FIG 10

PENDULAR BOND BETWEEN SPHERES



a RADIUS OF CURVATURE OF MENISCUS

b RADIUS OF RING OF PENDULAR LIQUID

θ SEMI ANGLE SUBTENDED BY MENISCUS

r RADIUS OF SOLID SPHERE

meniscus. The cohesive strength may fall with decreasing moisture content. Chromite grains are, however, fairly rounded in shape and this theoretical concept is, thus, applicable to this type of pellets, until further reduction of the moisture content creates no increase in the curvature of the meniscus to compensate for the decrease in the radius of the ring of pendular liquid.

The effect of water content on the compressive strength of chromite pellets was investigated experimentally. Pellets dried in still air at room temperature exhibited a gradual increase in compressive strength with decreasing moisture content as shown in Fig. 11. The maximum compressive strength occurred at an average moisture content of 7.8%. On further drying, the compressive strength decreased in agreement with the above theory.

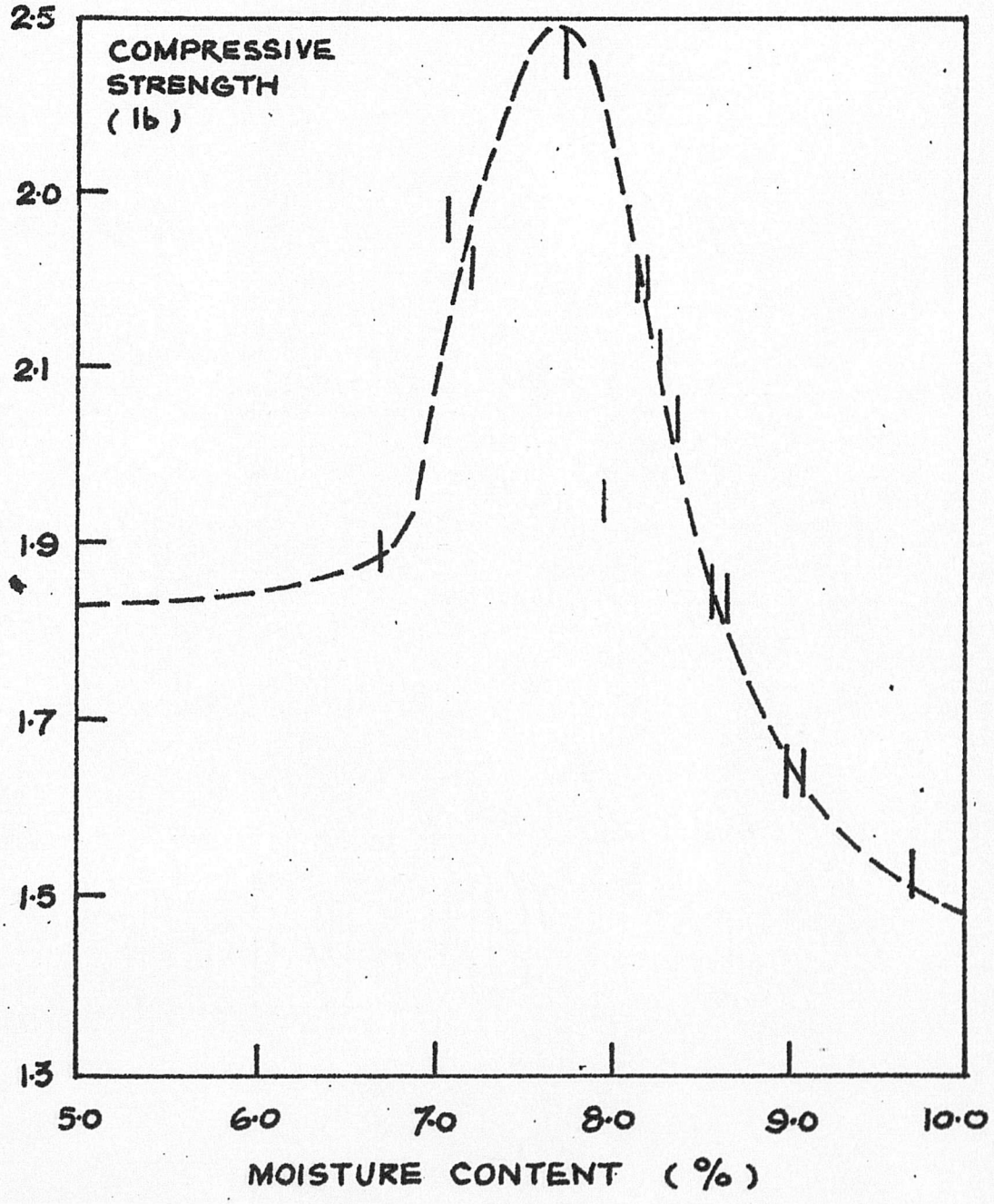
Physical interlocking.

Mechanical forces of cohesion arising from surface roughness and irregularity of the particles may cause physical interlocking on a scale ranging from macroscopic to submicroscopic.

Chromite grains commonly show fissures, cracks and protruding corners, although they are generally rounded in shape. In a pellet with particles lying in close proximity to one another, application of pressure may result in mechanical interlocking of particles and actual welding of points of contact. Firth (30) considered the compressive force exerted by a pellet resting entirely on a single grain. On account of the very small

FIG 11

EFFECT OF MOISTURE CONTENT ON STRENGTH OF PELLETS



areas of actual contact between grains, point pressures equivalent to several thousand p.s.i. were reported to be possible. In actual practice, a pellet is likely to lie on a group of grains instead of one grain at a time, but the pressure imparted is still high if the weight of a whole column of superincumbent pellets is taken into consideration. This suggests that pellets produced in a drum with a big load are stronger than pellets produced in a drum having a small load (see Table 10). Table 10 demonstrates the effect of drum loading on the compressive strength of the pellets, the moisture content of the pellets and the pelletizing time being the same in each test.

It may be seen that the compressive strength of the pellets rose as the load was increased from 800g to 1700g. Beyond a load of 1700g, however, weaker pellets were produced owing to excessive cascading in the drum.

During the process of rolling, pressure exerted on a pellet is transmitted from its surface to its core. The transmission of pressure is progressively reduced in accordance with the simple theory of transmission of pressure through a powder, so that particles at the surface of the pellet will receive a higher compressive pressure than those in the interior. In addition, successive layers are packed with increasing pressure during pelletizing because of the increasing weight of the growing pellet. The surface layer of a finished pellet is,

hence, most highly compressed. This phenomenon was frequently observed in dissected pellets during the course of the present investigation.

TABLE 10

Compressive Strength of ½" Pellets Produced in a Drum Having Different Total Loads

Total Load in Drum (g).	Seed Pellets in Load (%).	Compressive Strength (lb)
800	25	1.2
1200	25	1.2
1700	25	1.4
2200	25	1.4
800	40	1.3
1200	40	1.4
1700	40	1.6
2200	40	1.4
800	60	1.1
1200	60	1.3
1700	60	1.5
2200	60	1.5
800	75	1.1
1200	75	1.2
1700	75	1.3
2200	75	1.1

Diameter of Drum 14"
Speed of Rotation 34 r.p.m. (125'/min)
Pelletizing time 2 min.

Cementation by binding agents.

The presence of a binding agent may cause deposition of solids at points of contact between particles cementing them together. The strength of this type of bond depends on the physical nature of the solid deposited, as well as on the adhesion of the binding agent to the surface of the chromite grains. The weaker of the two links will be responsible for failure of pellets under compression. Hence the mode of deposition of the solid and the surface conditions of the chromite grains will contribute to the efficiency of this type of bonding. This aspect of the bonding mechanism is further discussed in section (6.4).

Forces of physico-chemical nature.

Specific forces of the ionic or homopolar type exist, but, because of their short ranges, they may be disregarded as granule-forming bonds. On the other hand, distances between surfaces of grains of the order of 100Å where van der Waals forces have still significant values, may occur in the granule complex. Of the several mechanisms of interaction included in the van der Waals forces only the London (69) (dispersion) force is additive for assemblies of atoms and can be invoked to account for adhesion. The attraction between two spheres has been calculated by Hamaker (68). To a first approximation, the force (F) in vacuo between spheres of radii R_1 and R_2, the surfaces of which are separated by a distance l is given by:

$$F = \frac{A\pi}{l^2} \cdot \frac{R_1 R_2}{R_1 + R_2}$$

where A is a constant having a typical value of 10^{-14} to 10^{-12} ergs. For particles of equal diameter the equation is simplified to:

$$F = \frac{A\pi}{l^2} \cdot \frac{R}{2}$$

Most of the chromite particles used in this investigation are of the order of 60μ , with only 0.6% of the particles having a diameter of under 5μ . Assuming a separation distance l to be 10Å, the force holding two particles of 60μ in diameter can be calculated to be of the order of 10^{-5} - 10^{-3} gram, which is greater than the weight of a particle (4×10^{-7} g).

The van der Waals forces have been considered by Rumpf (70) who showed that for particles of the order of 60μ, the capillary forces due to the presence of liquid responsible for the compressive strength of agglomerates was over 100 times that contributed by the London forces. In green pellets, the London forces can hence be neglected.

5.13 Effect of Rolling on Strength of Pellets.

Newly formed pellets were comparatively weak, and they failed to withstand compressive forces exceeding one pound. However, if they were subjected to further rolling in a drum, a considerable increase in strength occurred, accompanied by an

expulsion of moisture from the pellets (ref. Fig.18). The effects of finishing rolling were therefore further investigated.

Pellets of $-\frac{3}{4}" + \frac{1}{2}"$ diameter formed by adding water to 1.2 kilograms of dry material in the 14" pelletizing drum, were rolled in batches in the drum at 125'/min (34 rpm) for fixed periods and then removed for compressive strength determinations. The results are shown in Figures 12, 13, 14 and 15.

It was found that during the initial stages of rolling, the compressive strength of the pellets increased rapidly. After 10 min., further rolling provided no further gain in compressive strength. On the contrary, a slight decrease in compressive strength was observed up to a rolling time of 15 mins., but, further rolling then resulted in a rapid increase in the strength of the wet pellets. A compressive strength of 1.8 lbs. could be obtained after 25 min. of rolling.

The grains of a newly formed pellet were loosely packed. The first stage of strength increase during rolling can be attributed to compaction, i.e. progressively closer packing of grains in the pellets and reduction in voids. This, however, was accompanied by a rapid reduction in moisture content of the pellets (ref. Fig. 18, showing reduction of moisture content during the first 10 min. of rolling.) The simultaneous reduction in voids and moisture content could result either in an increase or decrease in the saturation of the voids, affecting the wet

EFFECT OF ROLLING ON WET STRENGTH OF PELLETS

FIG 12

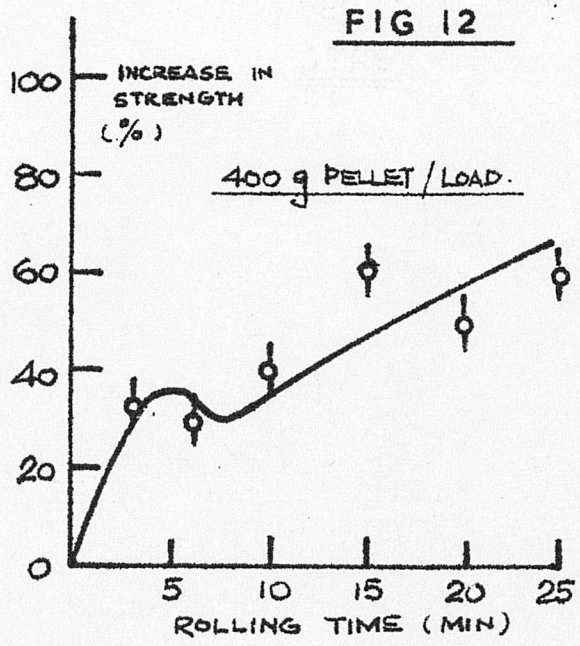


FIG 13

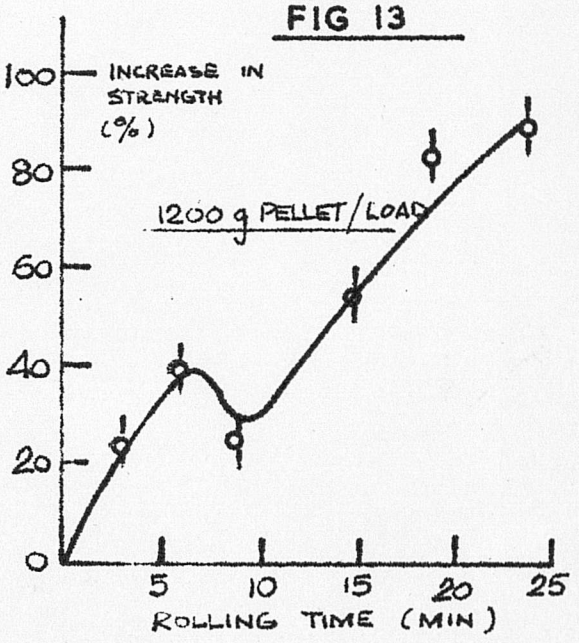


FIG 14

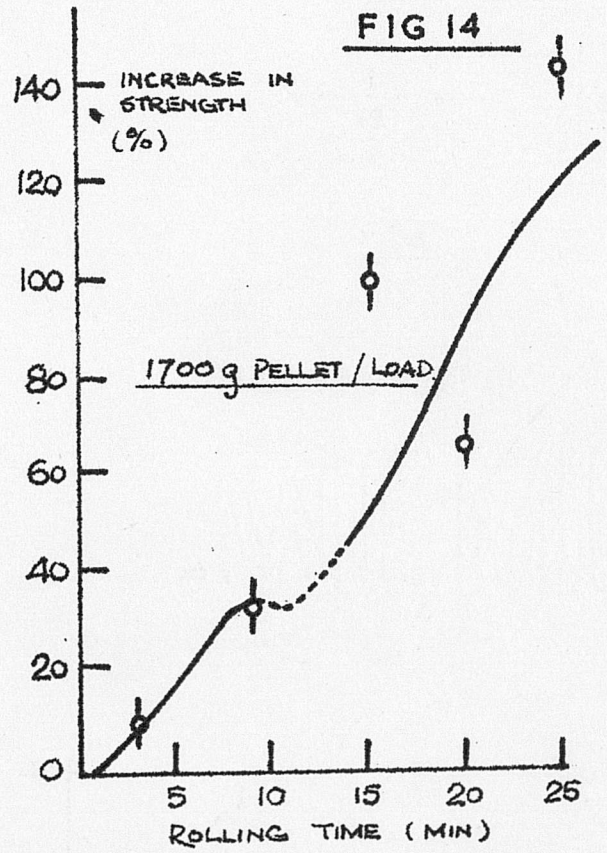
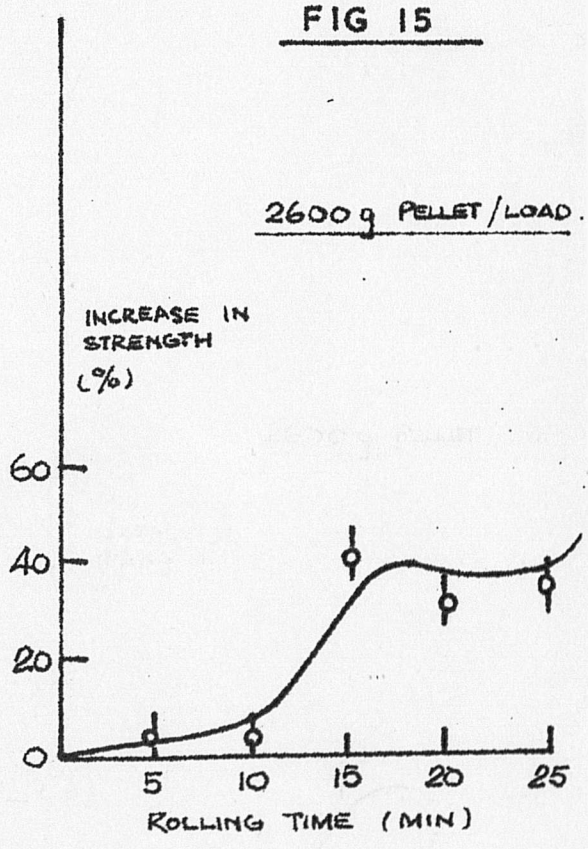


FIG 15



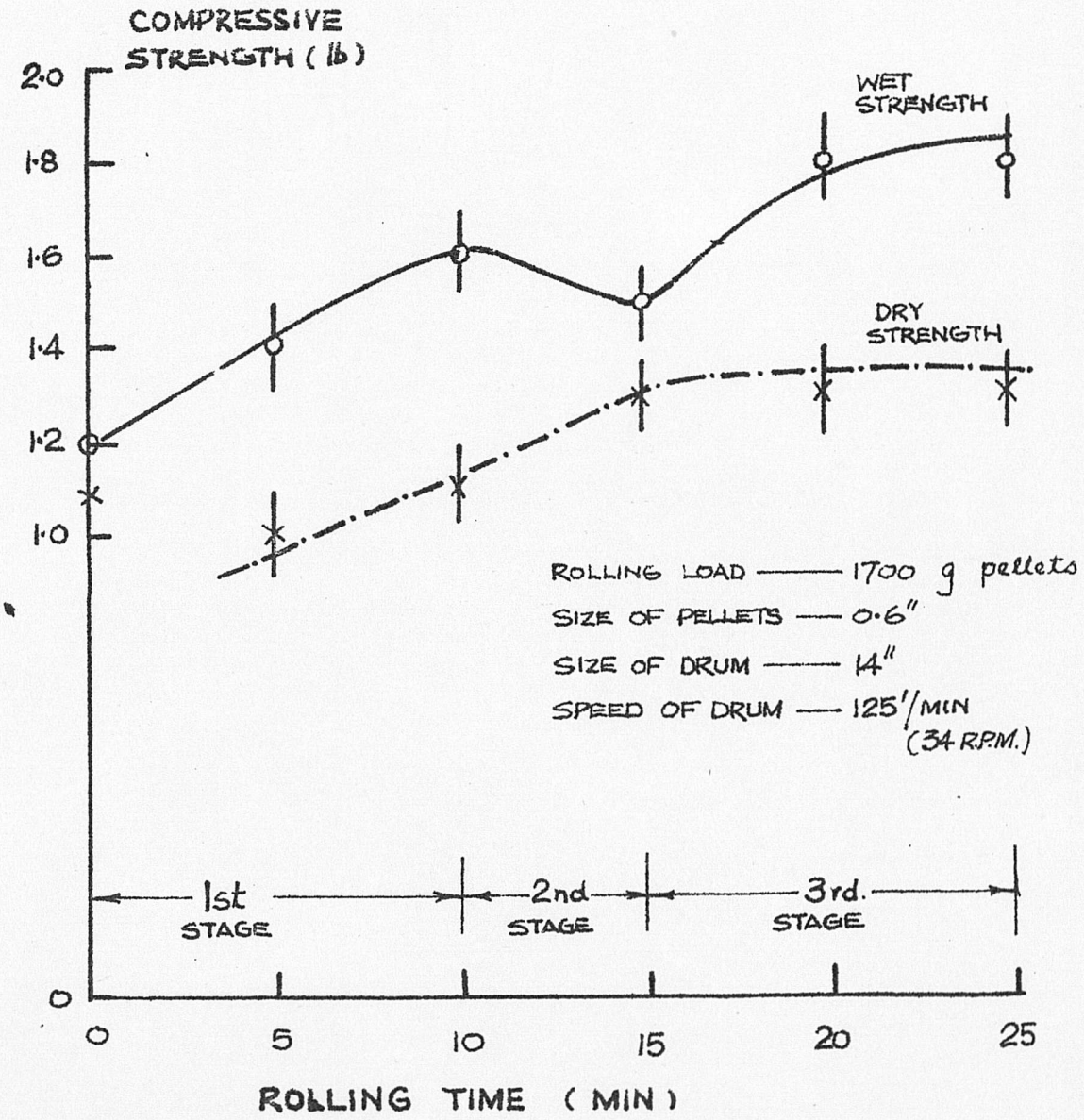
bonding of the grains directly. Fig. 16 shows that there is a constant difference between the wet and dry strengths of the pellets during the first 10 min. of rolling. If this difference were to be attributed mainly to the surface tension effect of the liquid, the saturation of water in the voids can be considered to be approximately constant. The increase in the green strength of the pellets at this stage is, therefore, mainly due to the increase in the co-ordination number, with more frequent mechanical interlocking of particles.

After the first stage of rolling, the rate of removal of water from the pellets becomes slow (see Fig. 13, showing slower rate of water expulsion after 10 mins. of rolling). However, the increase in dry strength still continues (see Fig. 16) while the green strength of the pellets is lowered (see also Figs. 12, 13, 14 and 15). Hence, it can be considered that the reduction in voids continues to proceed during the second stage of rolling while the saturation of the voids rises. A lowering of the compressive strength owing to the increase in void-saturation is, therefore, resulted.

When compaction has reached its limit under the given conditions in the drum, further rolling is still accompanied by slow removal of water. The saturation of the voids is once again reduced and the strength of the pellets therefore resumes an upward trend through rising surface tensional pull. The mechanism

FIG 16

EFFECT OF ROLLING ON WET & DRY STRENGTH OF PELLETS



in the last stage of rolling is indicated in Fig. 16. There is no increase in the dry strength of the pellets although the wet strength of the pellets rises rapidly with a longer rolling time. Surface tension is the chief factor contributing exclusively to wet strength. The relationship between pellet strength and rolling time can be regarded as being due to two separate super-imposed bonding mechanisms: bonding by pendular water and bonding by interlocking of particles in the pellets.

Fig. 17 shows a similar relationship between pellet strength and rolling time for pellets formed with wet material in the presence of seeds.

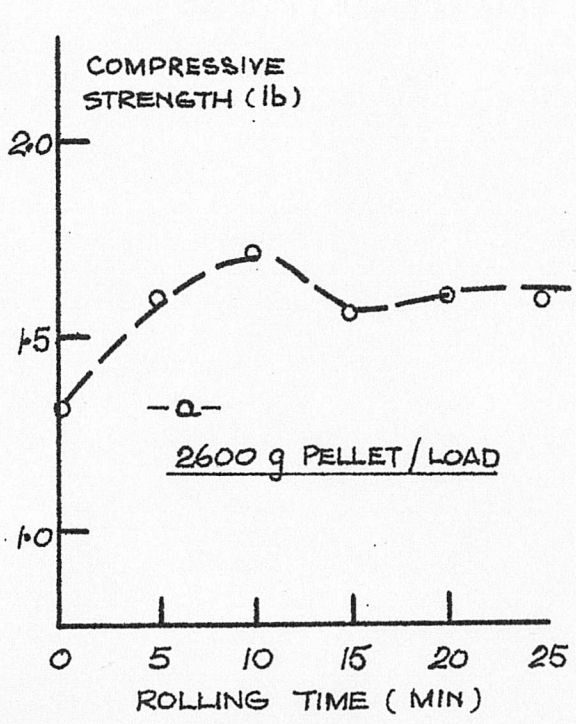
5.14 The Concept of Water Migration During Rolling.

The removal of water from the pellets during rolling and compaction is partly responsible for the increase in the green strength of the pellets. The mechanism of water removal therefore merits attention.

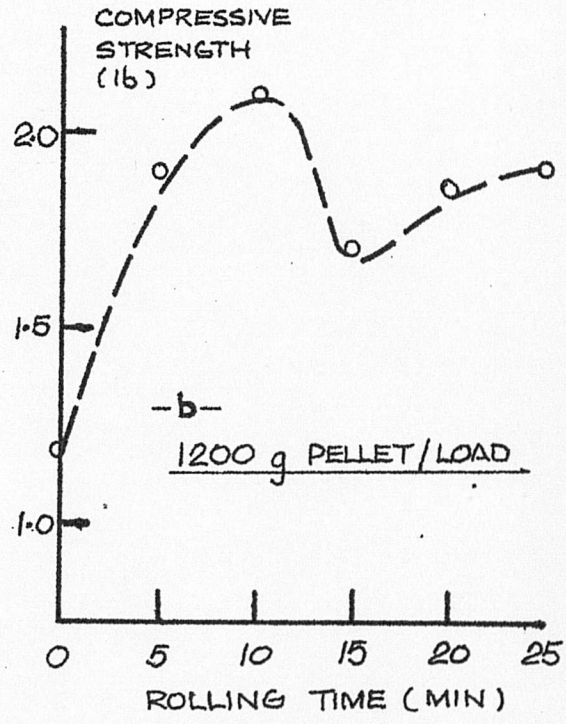
It was stated earlier that the water in the pellets is probably in a "funicular" state, with air partially occupying the voids of the pellets. This air could either be connected to the atmosphere through channels or form isolated air pockets, entirely surrounded by solid walls and water. During the initial stage of rolling, closer packing of the chromite grains occurs and owing to the process of rearrangement of the grains, the pellets tem-

FIG 17

EFFECT OF ROLLING ON WET STRENGTH OF PELLETS OBTAINED FROM A WET FEED



A



B

porarily expand in volume before contracting again to a new, closer state of packing. The voids in the pellets swell and shrink accordingly.

In the case of a pellet having almost all the voids saturated with water, but containing a few isolated air pockets, rolling caused water migration to the surface of the pellet where evaporation and transfer of moisture occur. If the wall of drum is drier than the surface of the pellets, the moisture will be picked up by the wall of the drum where evaporation will also take place. In addition the water can also be transferred to less water-saturated materials in contact with the pellets. The latter contributes to further pellet growth through picking up loose material on contact .

The movement of water is due to two factors:

1) Progressive compactions which squeeze out any excess moisture.

2) The centrifugal action produced by the rotation of the pellets during rolling.

Rolling induces an outward flow of water from the core to the circumference in the plane of rotation. This generates a region of low pressure at the core and, therefore, an inward flow of water along the axis of rotation of the pellet, i.e. at right angles to the plane of rotation. Changes in the plane of rotation occur owing to random rolling and collision with other

pellets. This causes corresponding shifts in the axis of rolling and, directions in the migration of water inwards along each new axis and outwards in the plane of rolling will also be affected. Continuation of this process of water migration creates more unsaturated channels and ultimately, movement of water to the surface will draw air inwards along the axis of rotation. When this stage is reached, the shell of the pellet shows a higher moisture content than the interior.

This process continues until maximum close packing is reached. Under the conditions of investigation, this state was normally achieved after 15 mins. of rolling and the corresponding bulk density of dry pellets was of the order of 2.8 g/cc. of pellet. At the state of close packing, the small mean diameter of the pores restricts movement of the remaining water which assumes a "pendular" state. High surface tension effect prevents complete removal of water from the core to the shell and evaporation should then occur throughout the pellet. This is faster at the surface than in the core, where the rate of evaporation would be limited by the rate of diffusion of water-saturated air to the exterior.

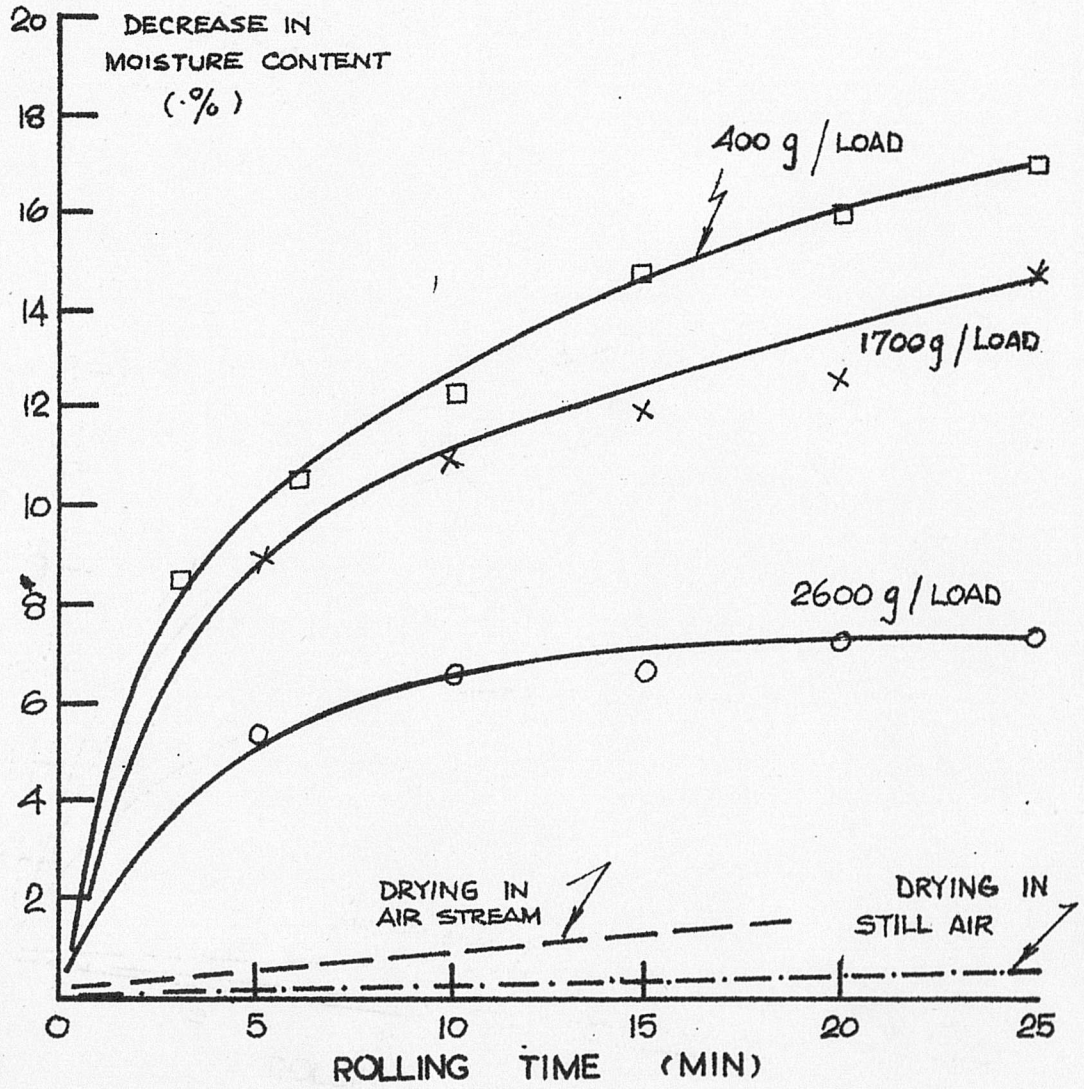
This concept of reduction of water content in the pellet was supported by experimental evidence of the changes in water content and distribution of water in the pellet during rolling. A load of pellets was subjected to rolling in the 14" drum rotating at a peripheral velocity of 125'/min. (34 rpm). The

average moisture content of the pellet was found to decrease rapidly during the initial 10 mins. of rolling (see Fig.18). After this period, the reduction of moisture content became slow, comparable to that of pellets drying in a gentle stream of air. The period during which the rapid decrease of moisture occurred, i.e. during the inital 10 min. of rolling (see Fig. 18) coincided with the period of rapid pellet strength increase during rolling, which also occurred during the first 10 min. (ref. Fig.16). The increase in the dry strength of the pellets was attributed to progressively closer packing of the grains and the same mechanism is held responsible for the rapid reduction of water in the pellets. Figure 18 also shows that the moisture reduction in a small load (400 g) was more rapid than that in a bigger load (2600 g). During rolling of the bigger load, it could be seen that only the pellets at the toe of the load rolled freely. Other pellets either tumble on one another towards the toe of the load or they are pinned to the wall of the drum by an overlying group of pellets. The drum with a small load imparted to each pellet more continuous rolling action accompanied by longer exposure to the atmosphere. This underlines the importance of rolling action of the pellet in the process of water reduction.

These pellets showed a difference in moisture content between the core and the shell. The shell was found to be more saturated. This phenomenon was further investigated.

FIG 18

EFFECT OF ROLLING ON MOISTURE CONTENT OF PELLETS



Hand moulded pellets, having a uniform moisture content were rolled in a drum. After rolling, the moisture content of each pellet was found to have decreased, but the shell had a higher moisture content than the core. The water appeared to have been redistributed within the pellets by gradual movement from the core to the surface where water could be removed. This continued until the average moisture content in the pellet was about 8.5% by weight. The movement of water from the core to the shell then stopped, drying took place more rapidly at the surface where the moisture content gradually fell below that of the core. This movement of water from the core to the shell was not observed during drying of the pellets in still air without rolling. The shell dried consistently at a higher rate than the core. Results of this part of the work are shown in Table 11. A similar effect was observed on rolling a cylindrical briquette on its axis in a drum. It was concluded that the movement of water from the core to the shell is attributable to the rolling action of the pellets.

TABLE 11.

Water Distribution in Core and Shell of Pellets

½" pellets air dried for 30 mins.		½" pellets rolled for 20 mins.		½" pellets, rolled for 15 min, and then air dried for 20 mins.		¾" pellets rolled for 20 mins.	
Shell	Core	Shell	Core	Shell	Core	Shell	Core
10.4% H_2O	11.2% H_2O	8.6% H_2O	8.4% H_2O	7.0% H_2O	7.5% H_2O	8.3% H_2O	8.0% H_2O

Initial moisture content of pellets : 12.0%

5.15 Effects of Drum Diameter and Velocity on the Strength of Pellets.

For the purpose of this investigation, 1.2 kilogram of $-\frac{3}{4}" + \frac{1}{2}"$ pellets were rolled for 5 min. and 20 min. in the 17", 14" and 12" steel drums. The values of the compressive strengths are shown in Table 12.

TABLE 12

Effect of Drum Diameter on Strength of Pellets During Rolling

Rolling load - 1200 g. $-\frac{3}{4}" + \frac{1}{2}"$ pellets - dry basis

Peripheral velocity - 125'/min.

Length of drums - 1 foot

Drum Diameter	17"	14"	12"
Load in kg./foot drum diam.	0.70	0.86	1.00
Percentage increase in strength after 5 min. rolling	35	40	40
Percentage increase in strength after 20 min. rolling	55	80	85

Earlier in this work, it was reported that a 14" drum, rotating at 125'/min. (34 rpm), required a load of 1.7 kilogram (dry basis) of $-\frac{3}{4}" + \frac{1}{2}"$ pellets to produce the best effect in imparting compressive strength to the pellets. This load corresponds to 1.2 kilogram of pellets per foot diameter per foot length of the drum. A larger or smaller load employed during rolling

tended to produce weaker pellets. The present series of tests again showed that the closer the load approached 1.2 kilogram/ foot diam. per foot length of drum, the greater was the pellet strength. The diameter of the drum alone had little apparent effect in this respect.

The optimum increase in strength obtained by rolling a load approaching 1.2 kilogram/foot diam./foot length of drum can be explained as follows. A small load (under 1.2 kilogram/foot diam./foot length of drum) does not exert sufficient pressure on the pellets to cause adequate interlocking and welding of the grains. A larger load provides higher compression to the pellets at the bottom of the load resulting in greater strength increase. However, for loads over 1.2 kilogram/foot diam./foot length of drum, cascading action is induced. This weakens the pellets and lowers their resistance to compression.

The effect of the peripheral velocity of the drum on the strength of the pellets was investigated using a 14" diam. drum. Charges of 1.7 kilogram of pellets were rolled at 20, 27, 34 and 41 rpm. for fixed numbers of revolution. The compressive strength of the pellets are shown in Table 13.

TABLE 13

Effect of Peripheral Velocity on Compressive Strength of Pellets During Rolling*

angular velocity / peripheral velocity		20 rpm 75 '/min.	27 rpm 100 '/min.	34 rpm 125 '/min.	41 rpm 150'/min.
Percentage increase in compressive strength after	170 revs	12	37	28	-
	680 revs	36	46	67	25

* Original compressive strength of pellets 1.1 - 1.2 lbs.

The best increase in strength of the pellets was observed at a peripheral velocity of about 125'/min. Higher or lower velocities gave weaker pellets; higher velocities caused the pellets to cascade while lower values showed progressive failure to lift the load high enough for efficient rolling.

It is concluded that the main factor responsible for the increase of strength is rolling the load without cascading. This is governed essentially by the load in the drum and by the peripheral velocity. However, for the purpose of rapid removal of water during rolling, the load in the drum should be small. It may be stipulated, therefore, that rolling with a relatively high load for rapid compaction followed by rolling with a small load for water removal will give the best finished product under any set of conditions.

5.16 Drying of Pellets.

Drying of pellets in still air was found to be very slow. Most water was lost from the shell of the pellets. (Reduction of average moisture content by 1% was achieved after 25 min. drying). During this process, water menisci at the surface of the pellets retreat inwards, towards the more restricted cross sectional areas of the capillaries. This causes an increase in the curvature of the menisci of water in the channels. The surface tension force is thereby increased and is responsible for pulling the water from the larger capillaries to the smaller ones until eventually all the remaining water is collected round the points of contact between particles. On further drying, this pendular water shrinks further towards the actual points of contact of the particles and, if a soluble salt or a fine suspension is present in the liquid, saturation is reached as evaporation proceeds and the deposition of solids occurs.

The process of drying is, however, complicated by the fact that as evaporation proceeds the surface tension of the liquid may rise. Since evaporation occurs more rapidly at the surface of the pellet a concentration gradient and hence, a surface tension gradient is created. It is suggested that, aided by capillary action, the surface tension gradient can induce a slow creep of water to the surface of the pellet along the channels and solid surfaces of the pellet. Eventually the point of

saturation is reached and salt is deposited at the surface of the pellet, increasing the surface tension of the liquid in contact with it still further. The deposition of salt provides numerous capillaries between the salt crystals and thus encourages capillary action. More salt-bearing liquid then moves to the surface and deposits more salt as it evaporates. Continuation of this process leads to a visible accumulation of salt at the surface of the pellet. This phenomenon is specially marked when drying takes place slowly in air but is less apparent on rapid heating. This may be due to the fact that "creeping" of the solution proceeds rather slowly so that on rapid drying the deposition of salt is more evenly distributed throughout the pellet.

The dried pellets are comparatively weak and are easily abraded. Firing to a high temperature is necessary for the provision of higher strength and abrasion-resistance for subsequent treatments in this beneficiation process.

6.0 HARDENING

6.1 Introduction.

The strength of a green pellet is partly due to the surface tension of the interstitial liquid and partly to the intimate interlocking of particles as discussed in section 5.12. However, the liquid is ultimately removed from the pellet by drying and when this stage is reached, the bonding forces due to the presence of the liquid disappear. The pellets become brittle and are easily abraded. Even before drying, the wet strength of pellets is inadequate for repeated handling, stockpiling or shipment. It is normal practice, therefore, to subject pellets to some form of heat treatment which imparts to them crushing strength of the order of hundreds or thousands of pounds.

In the present work, firing serves the dual purpose of hardening the pellets through sintering at a high temperature and of reducing the iron in chromite to an acid-soluble state.

The mechanism of sintering.

Sintering is a thermal treatment of a loose or compacted aggregate of fine particles for the purpose of producing large and physically strong agglomerates by causing welding of particles to each other. This process can be applied to a homogeneous material e.g., sintering of pure metal powder or to a heterogeneous substance e.g. sintering of ores. Jones (71) suggested that the mechanism of the sintering of a homogeneous metal powder could be generalised as a sequence of two phenomena:

(a) adhesion and welding of surfaces at points of

actual contact and (b) change in shape of the particles to provide stronger joints. Without (a) there is no sintering and without (b) there is no densification.

Thomas (72) postulated that the material at the points of contact has been subjected to high pressures at one stage or another. Localised deformations are thus invariably present and a state of high energy exists. In consequence, there is a tendency for the dislocated atoms to rearrange themselves until a lower energy state is again reached. Diffusion and recrystallisation at the points of contact will, therefore, proceed whenever atomic mobility permits.

At room temperatures, the mobility of the atoms is low and the process proceeds slowly. At higher temperatures and with increased mobility, diffusion and recrystallisation may occur rapidly, resulting in a sharp increase in pellet strength. At the same time the surface energy of the particles also tends to decrease to a lower value owing to the reduction in surface areas of the grains. The irregular surfaces of the particles become smoother and the particle shape less angular. Smaller grains coalesce to form bigger particles initiating welding and grain-growth.

Rhines and co-workers (73) suggested that the process of welding and grain-growth is partly due to an evaporation-condensation process in which the vapour pressure of the material

at the convex surfaces of the grains is believed to be lower than that at the concave surfaces. Sublimation at high temperatures can, therefore, occur resulting in an increase in thickness of the welded joints at the points of contact. This mechanism was also held responsible for the formation of smoother surfaces of the particles.

The process of sintering is normally accompanied by densification of the aggregate through reduction in voids as well as through redistribution of material in the compact. Investigations of the process of redistribution in the field of powder metallurgy have led to the observations of various mechanisms including grain boundary diffusion (74, 75), bulk diffusion (76, 77), plastic flow (78) etc. In the case of sintering heterogeneous materials like ores, another mechanism of sintering should also be considered. Sufficiently high temperatures may cause the formation of a liquid phase which, on cooling, solidifies to provide bonds contributing on the high fired strengths of the sinter.

Factors influencing sintering behaviour have been investigated empirically in the treatment of materials such as alumina (79), nickel oxide (80), quartz (81), sodium chloride (82) etc., and a great volume of literature has been published on the sintering of iron ores and iron ore pellets.

Holowaty, Goldfein and Sheets (83) studied the influence

of the characteristic of the feed on the production rate of sinter in the sintering of iron ore, & Wild and co-workers (84, 85, 86, 87) examined the fundamentals of sintering and their application to the industrial sintering processes. Their investigations include the rate of heat transfer, the relationship between sinter strength and temperature history, pressure gradient through the sinter bed etc., while the mechanisms and kinetics in commercial sintering practice were examined by Davis and Mitchell (88).

Investigating the sintering of magnetite pellets under reducing conditions, Cooke and Stowasser (40) observed recrystallisation of the magnetite grains and slag formation as bonding mechanisms in fired pellets. Under oxidizing conditions, however, haematite grains were produced and hardening was found to be due mainly to diffusional bonding of these haematite particles. No slagging was observed and the increase in strength of the pellet was greater than that fired under reducing conditions. These observations were supported by the findings of Cooke and Ban (37) who also obtained stronger taconite pellets under oxidizing conditions. Through studying the microstructure of the pellets they reported (51) that slag bonding, diffusion, recrystallization and crystal growth were possible mechanisms of sintering. Similar mechanisms of sintering were also reported by Urich and Han (45) who noted that small grains gradually disappeared to form bigger

ones during the process of hardening. The mechanism of sintering of iron ore pellet was further investigated by Ridgeon, Cohen and Lang (43), using haematite pellets. It was concluded from X-ray microradiography (57) that under oxidizing conditions the pellets were hard but the porosity of the pellets was not increased. The haematite flakes were observed to recrystallise and shrink, resulting in a highly porous structure. Firing under reducing conditions, on the contrary, led to the formation of closely packed equiangular magnetite grains. The porosity of the pellets was reduced and fusion of adjacent pellets into large aggregates was a risk necessitating a high degree of temperature control. No changes in the microstructure were observed when a small amount of inorganic binder was incorporated in the pellets.

In the hope of achieving greater economy through reduction in fuel consumption at lower firing temperatures, and in order to improve the smelting behaviour of 100% pellet burden in blast furnaces, attempts have been made to incorporate fluxing agents in the pellets. Merklin and De Vaney (52) used dolomite as a flux for taconite pellets but reported that the addition of dolomite alone resulted in weaker pellets. This contradicts the findings of Limons and Kramer (39) who employed dolomite as a fluxing agent in the sintering of iron ore. In the presence of bentonite clay and soda ash, however, Merklin and De Vaney (52) found the fired strength of the fluxed pellets to increase,

accompanied by extensive shrinkage. Limestone and borax were used by Ban and Erk (41) who reported an improvement in the quality of pellets. On the other hand, Rovenski (90) found that a high degree of disintegration occurred on drying pellets containing lime as fluxing agents.

A major disadvantage in the addition of fluxing agents lies in the increase in fusion and slag sealing the voids in the pellets after firing. In the case of iron ore sinters, the efficiency of the gas-solid reaction is reduced (91) and for chromite pellets this would obstruct the penetration of acid during leaching of the reduced iron.

No reference has been found in existing literature to the sintering of chromite pellets. Owing to the high melting point of chromite and small amounts of associating gangue (mostly serpentine), formation of slag is likely to be a subordinate factor in sintering such pellets. Diffusional bonding of chromite appears to necessitate high temperatures. Oxidizing conditions are not available and selective reduction of iron oxide is a necessary condition for the subsequent leaching stage. The problems and mechanisms of hardening chromite pellets are thus very different from those of the apparently similar process of sintering iron ores.

6.2 Importance of Using a Binder.

When all the moisture in pellets has evaporated and before high-temperature bonding is reached, the pellets are weak and have low resistance to impact, compression and abrasion. Incorporation of a suitable binder normally helps to provide the pellets with sufficient strength in the dry state. It also prevents the disruption of pellets during rapid drying.

When green pellets are dried rapidly, steam is generated and if its escape is obstructed explosive disruption of the pellets can occur. Sewerynski and Wlazinska (56) reported that iron ore pellets consisting of very fine particles had to be dried very slowly and carefully in order to prevent disintegration, whereas, green pellets consisting of larger particles could be placed directly in an oven heated to 800°C without any bursting of pellets. In the presence of a suitable binding agent, however, even fine-grained pellets could be dried more rapidly without much disintegration.

A binder, thus, has two functions:

(1) To prevent disruption by steam during drying, and

(2) To raise the dry strength of the pellets.

However, it must also be taken into consideration that addition of a binding agent can alter the behaviour of the pellets at high temperatures during sintering and this may lead to a change in fired strength.

6.3 Binders Used in Pelletizing Processes.

Cooke and Stowasser (40) investigated the use of sodium fluoride, lime and magnesium oxide as binding agents. They reported that the first two additives did not prevent disintegration of pellets while magnesium oxide yielded no improvement in pellet strength. Lime, however, promoted the oxidation of magnetite to haematite. This was attributed to the preservation of permeability in pellets by lime, facilitating gas-solid reaction, thus, resulting in more efficient oxidation. The addition of lime as a binder was also advocated by Sewerynski and Wlazinska (56) who found that the addition of lime could be used to lower the operating temperature during sintering . This was believed by Ban and Erk (41) to be due to the formation of solid solutions of CaO, SiO_2 and Fe_2O_3 and calcium ferrite. Calcium chloride was tried by Krotkiewski and Sewerynski (92) who reported that this binder increased the dry strength of the pellets.

Another binding agent commonly used in pelletizing iron ore is bentonite clay (26). Ban (60) and Ban and Erk (41) reported that bentonite improved the green, dry and fired strength of pellets and Ridgeon, Cohen and Lang (43) attempted to assess systematically the suitability of various binding agents for the pelletizing of flaky haematite. Their investigation included a variety of organic as well as inorganic compounds. Among the organic compounds investigated were starch, dextrin, sulphite

lye and alginate products. These binding agents were found to burn out at temperatures well below those at which high temperature bonding could be reached and their usefulness was, thus, very limited. Inorganic salts that proved more effective included sodium hydroxide, sodium carbonate, potassium carbonate, calcium chloride, magnesium chloride and magnesium sulphate. All of these were found to yield a marked improvement in the dry strength of the haematite pellets. No conclusions regarding the mechanism of the binding action were drawn from the investigation, and it was not discovered whether interactions with the binding agents concerned the haematite or the quartz gangue.

Binding agents have also been employed in other pelletizing industries. Lang and Carveth (93) found that an asphalt binder was required to pelletize coal fines, and Sherwin and Stevenson (50) reported the importance of soluble salts in the balling of fertilizers. In investigating the pelletizing in cement industry, Tonry (94) studied the use of starch, calcium chloride, waste sulphite product, sodium silicate, bentonite, etc., as binding agents.

6.4 Binding Agents Investigated in this Project

A major purpose of binder addition in this work is the prevention of disruption of pellets during rapid drying. This is a pre-requisite of high fired strength and was therefore investigated. In this connection, the suitability of various

common inorganic compounds as binding agents was examined. The present investigation included the testing of hydroxides, fluorides, carbonates, chlorides, sulphates, sodium cyanide, sodium silicate, and bentonite clay.

Effect of binders on the prevention of distruption during rapid heating.

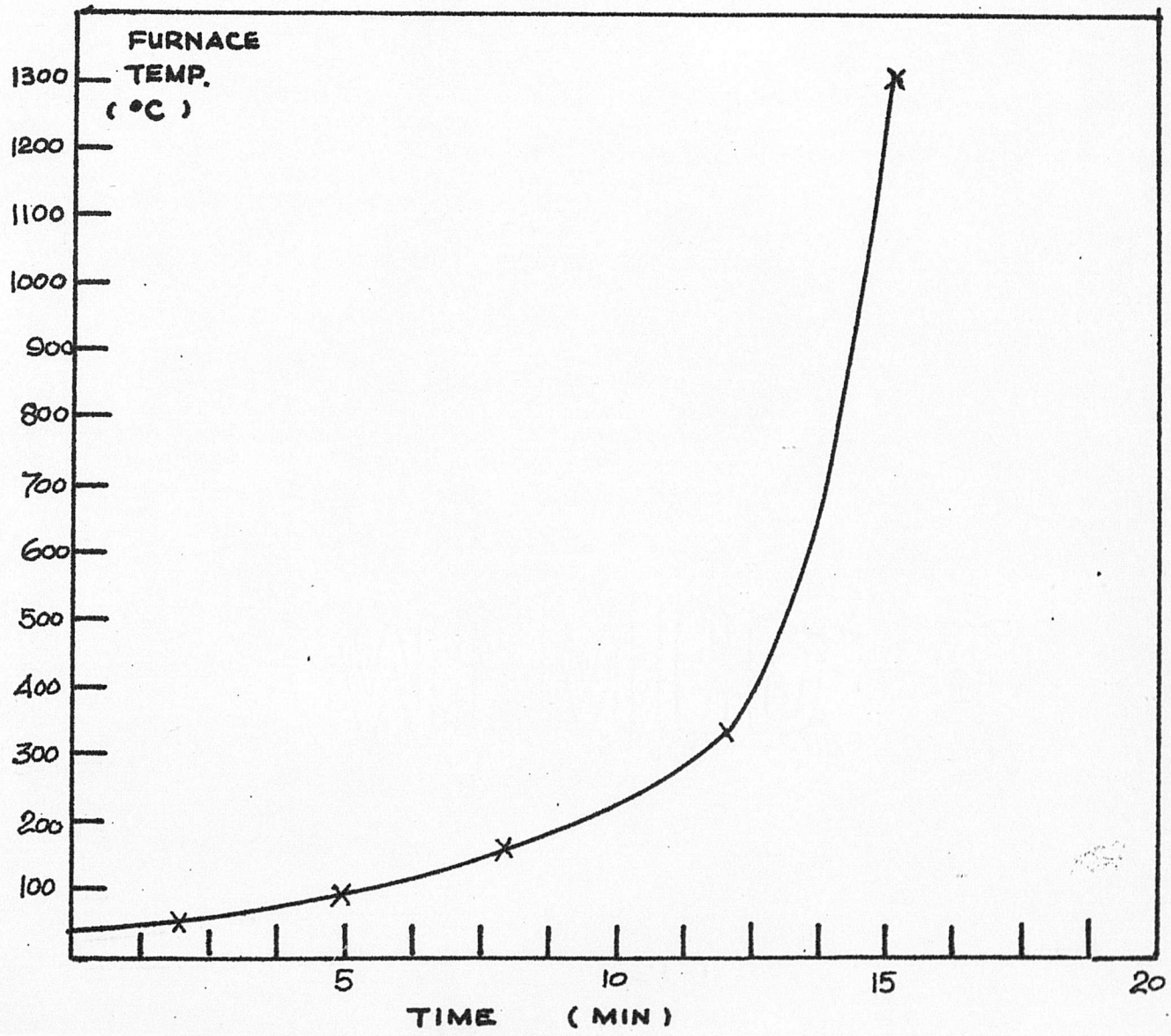
Various proportions of selected binding agents were added to batches (1.2 kilogram/batch) of dry material in the 14" drum. Pellets were prepared by identical 2 min. rolling, rotating at 34 r.p.m. as described in section 5.5. The $\frac{1}{2}$" pellets thus formed, were removed without further rolling and were rapidly heated in a horizontal platinum tube furnace in an atmosphere of nitrogen. The rate of heating is shown in Fig. 19.

Each batch was represented by 5 pellets on which visual observations were made to assess the effectiveness of the binders to prevent disruption.

Water and solutions of hydroxides, fluorides, carbonates and cyanides all failed to produce pellets surviving breakage before high temperature bonding was reached. Sodium chloride, sodium sulphate, ferrous sulphate, sulphuric acid and bentonite clay were found to be efficient. Of these, sodium chloride, sulphuric acid, bentonite clay and sodium carbonate were further investigated to ascertain their suitability as a binding agent in the wet, dry and fired state. The comparative performances

FIG 19

RATE OF HEATING OF PELLETS IN THE HORIZONTAL PLATINUM TUBE FURNACE



of binders in the prevention of breakage during rapid drying are shown in Table 14.

For this purpose chromite briquettes of 1 inch diameter and 15.0 gram in weight, were used. The briquettes were made by compressing fine concentrates containing 9.3% moisture, graphite and an appropriate binding agent in a cylindrical steel mould in a Millen Mounting Press, up to a pressure of 5000 lbs p.s.i. which was maintained for 5 sec. before the briquettes were ejected. The wet strength of briquettes was tested by radial compression using the Millen Mounting Press or the Salter Compression tester, as soon as the specimen was produced. For dry strength determination the briquettes were dried in an electric drying oven at 150°C for 12 hours. For the determination of fired strength, specimens were prepared by firing dried briquettes in a horizontal platinum tube furnace in an atmosphere of nitrogen to a temperature of 1340°C. The rate of heating was set at 700°C/15 mins. up to 700°C and then at 500°C/hour up to 1340°C. The maximum temperature was held for 5 min. and the briquettes were then withdrawn to the mouth of the tube to cool in an emerging stream of nitrogen before being exposed to atmosphere. Radial compressive strengths were determined in the Millen Mounting Press and the results are shown in Tables 15 and 16.

TABLE 14

Selection of Binding Agents.

Binding Agents / Conc. of Solution	20%	15%	10%	5%	Comments
Water			x		
NaCN			x	x	
Na_2CO_3	x	x	x	x	
NaCl	#	#	#	x	
Na_2SO_4		#	#	x	Cracked, fused together and to container
NaF	x		x	x	
NaOH	x	x	x	x	
$NaSiO_3$	0	0	0		
KCl	#	#	0	0	
$CaCl_2$	0	0	0		
$Ca(OH)_2$	x	x	x	x	
$MgCl_2$	x		x	x	
$BeCl_2$	x		x		
$Cr(NO_3)_3$	0		x		
$CrCl_3$	0	0	0	x	
$FeCl_3$	0		x	x	Pellets very brittle
$FeSO_4$	#	#	#	x	
H_2SO_4	#	#	#	#	Sacked, fused together and to container with -15% soln.
HCl	0	0	0	0	Pellets very brittle
$Na_2Cr_2O_7$	x		x		
Borax		#	0	x	
0.5% Bentonite Clay		#			

SYMBOLS: # = Good cohesion
0 = Partial disintegration during heating
x = Complete disintegration

TABLE 15

Compressive Strength of 1" Chromite Briquettes

Binding Solution	Wet Strength (lb)	Dry Strength (lb)	1340°C Fired Strength (lb)
Water	15	10	250
0.5% bentonite + water	15	25	1000
5% Na_2CO_3 solution	15	20	800
5% NaCl solution	15	20	1000
3% H_2SO_4 solution	15	40	1500
3% NaCN solution	15	40	800

Effect of binders on wet bonding.

Table 15 shows that there was no significant difference between the wet strengths of briquettes made with various binding solutions. The concentration of solutions containing the various binders were of the order of 5%. Little change on the value of surface tension of water was expected, and consequently, the wet bonding of particles by an interstitial liquid would not differ greatly.

Effect of binders on dry bonding.

Table 15 also shows that the dry strength of the briquettes was lower than the wet strength in the absence of a binding agent, in accordance with the observation in section 5.13. However, the incorporation of a binding agent increased the dry strength. In this respect bentonite clay and sulphuric

TABLE 16

Compressive Strength of 1340° C 1" Chromite Briquettes Made With Different Binding Agents and Different Graphite Addition

1.	Effect of graphite on strength with H_2O binder	Percentage C by weight	8	4	2	0
		Compressive strength (lb.)	700	800	800	250
2.	Effect of graphite on strength with H_2O + bentonite	Percentage C by weight	-	4	2	0
		Compressive strength (lb.)	-	1350	1250	1050
3.	Effect of graphite on strength with 3% NaCl + bentonite	Percentage C by weight	-	4	2	0
		Compressive strength (lb.)	-	800	500	450
4.	Effect of graphite on strength with 3% H_2SO_4	Percentage C by weight	-	4	2	0
		Compressive strength (lb.)	-	1450	1000	1100
5.	Effect of H_2SO_4 conc. on strength of specimen with 2% graphite	Solution concentration	3%	2%	1½%	0%
		Compressive strength (lb.)	1000	700	500	800
6.	Effect of H_2SO_4 conc. on strength of specimen with 2% graphite and bentonite	Solution concentration	3%	2%	1½%	0%
		Compressive strength (lb.)	650	650	650	1250
7.	Effect of NaCl conc. on strength of specimen with 4% graphite	Solution concentration	5%	3%	1½%	0%
		Compressive strength (lb.)	1000	900	500	800

acid were more effective than sodium chloride and sodium carbonate (see Table 15).

The difference in the effectiveness of various binders in the dry bonding of chromite particles was not apparent. For the purpose of obtaining better understanding of different mechanisms of dry bonding, qualitative microscopic observations were made on the drying of various binding solutions on a flat surface of a large lump of chromite ore.

It was observed that the salt crystals (sodium chloride or sodium carbonate) deposited by the evaporation of the binding solution were of various sizes depending on the rate of evaporation. Slow evaporation resulted in the formation of large salt crystals on the surface of the ore. Little adhesion to the chromite surface was observed and there was no salt crystal growing into or deposited in the cracks of the ore specimen. On the other hand, more rapid evaporation produced a large number of small cohesive crystals depositing on the surface as well as in the cracks of the ore. These crystals were found to be more difficult to remove. The main bonding mechanism between the salt and the ore was therefore considered to be the deposition of salt in the cracks, resulting in mechanical bridging and interlocking.

Observation on the drying of a bentonite clay suspension revealed that the clay particles were invariably deposited on the surface as well as in the cracks of the ore independent of the

rate of drying. Mechanical removal of the deposited clay was found difficult, indicating strong bondings between the clay and the ore.

However, if the surface of the ore was contaminated with grease, deposited salt or bentonite clay due to slow drying was observed only on the superficial surface of the ore. There was no adhesion or interlocking and the deposited solids fell off readily.

Evaporation of a drop of 10% sulphuric acid on the surface of a polished specimen of chromite ore was also observed under a microscope. It was found that the surface of the ore which had been in contact with the acid became brighter and a residue of very small colourless salt crystals were deposited on the surface of the solid at the edge of the original drop of acid, indicating the dissolution of material into the acid and the re-deposition of salt on its complete evaporation. The dry bonding of sulphuric acid can therefore be considered to be due to the cementing action of salt on chromite particles which had been cleaned by the corrosive action of the acid. An efficient dry bonding of chromite particles when sulphuric acid was used as a binder could therefore be expected, (see Table 15)

The effectiveness of a binder in the dry bonding of chromite particles could hence be attributed to (a) the mode of deposition of solid from the binding solution, (b) the nature

of the binder and (c) the cleanliness of the surface of the chromite.

Effect of binders on bonding at high temperatures.

The behaviour of binders at the temperature of sintering is of complex nature. With the exception of bentonite clay, all the inorganic materials tested would have evaporated at 1340°C unless reacted chemically with the ore to form a compound having higher temperature of evaporation. The fired strength of the briquettes would hence be unaffected by a binder. It would be due mainly to the welding of chromite particles and/or the formation of phases of glassy or crystalline structure. However, in this test work, it was found that different binders produced briquettes with different compressive strengths (see Tables 15 and 16).

Tables 15 and 16 show the order of magnitude of increase in strength due to binders, when firing was taken to 1340°C. The strength increase was especially favourable with bentonite clay as binder (compare runs 1 and 2, Table 16). However, the efficiency of this binder was appreciably decreased by the presence of a small amount of sodium chloride or sulphuric acid (see runs 2, 3 and 6 in Table 16) which reduced the fired strength of briquettes from the order of 1300 lb. to about 700 lb.

The use of sodium chloride or sulphuric acid alone as binders brought a lowering of the fired strengths of the briquettes. This was more apparent when a 1½% concentration of solution was used for the moulding of green briquettes, but at higher concentrations

of binding solutions, the fired strengths of the briquettes were again raised. (See runs 5 and 7, Table 16). The fired strengths obtained with a 5% sodium chloride solution or a 3% sulphuric acid were comparable to that reached with a bentonite binder (see Table 15). Fired strengths of briquettes made with sodium cyanide and sodium carbonate were lower (800 lb.) while the fired strength of briquettes with no binding agent was only 250 lb.

Qualitative analysis (96) of the gas emerging from the furnace used for firing chromite briquettes containing sodium chloride and graphite in an atmosphere of nitrogen, showed the absence of carbon dioxide, but at temperatures above 800°C silicon, chloride, hydrogen sulphide and traces of iron and aluminium were detected, indicating complex chemical reactions.

6.5 Sintering of Chromite Concentrate Under Reducing Conditions.

The mechanism by which sintering of chromite concentrate occurs has not been reported in existing literature. The present work was, therefore, directed towards investigating the sintering of chromite pellets at various stages of firing and to a further understanding of the mechanism of the process. The microstructure of the reduced ore pellets was examined by microradiographic techniques and reflected light microscopy.

The preparation of specimens for microradiography and for reflected light microscopy necessitated the impregnation of the porous agglomerates to avoid excessive fragmentation and grain loss

during grinding and polishing. Damar gum was generally satisfactory for this purpose.

For microradiography of thin sections, copper K_α radiation was used at 40 K.V. and 10 m.A. following the technique described by Cohen (95). Copper K_α radiation is heavily absorbed by iron and chromium and little absorbed by all other elements present in the pellet section. The absorption is independent of the state of chemical combination and depends only on the number of iron and chromium atoms present. In the radiographs material rich in iron and chromium therefore appears light, material free from iron and chromium and holes in the section appear black, and greys represent material having intermediate iron and chromium contents, e.g. chromite or gangue containing iron.

In this investigation $\frac{1}{2}$" chromite pellets containing sodium chloride as binder and a various amount of graphite were prepared by rolling in a 14" drum as described in previous cases ref. section 5.5). They were then dried and fired rapidly in an atmosphere of nitrogen to different temperatures for five minutes, cooled in a neutral atmosphere to room temperature and then subjected to compression tests. The results are shown in Table 17.

TABLE 17

Compressive Strengths of Pellets Sintered to Various Temperatures

% Graphite in pellets	4		2		0	
Conc. of NaCl Soln	5%	3%	5%	3%	5%	3%
Wet Pellets	0.5 kg	0.4 kg	0.5 kg	0.4 kg	0.6 kg	0.5 kg
100°C	0.5 kg	0.4 kg	0.6 kg	0.4 kg	0.6 kg	0.5 kg
400°C	0.7 kg	0.5 kg	0.6 kg	0.6 kg	0.8 kg	0.7 kg
800°C	1.1 kg	1.4 kg	1.6 kg	2.1 kg	2.3 kg	2.6 kg
1000°C	3.2 kg	6.5 kg	4.6 kg	8.0 kg	8.4 kg	9.2 kg
1200°C	20.0 kg		24.0 kg		29.0 kg	
1300°C	40.0 kg		38.0 kg		30.0 kg	
1340°C	55.0 kg		50.0 kg		45.0 kg	

Effect of Graphite on Strength of Pellets:

Table 17 shows that the presence of graphite has a deleterious effect on the wet strength, dry strength and semi-fired (below 1000°C) strength of the pellets.

The decrease in the wet strength of the pellets can be attributed to hydrophobic properties of the graphite particles resulting in difficult wetting and hence, less effective bonding by the interstitial liquid. Similarly, the decrease in dry strength in the presence of graphite can also be attributed to less efficient cementation of particles with hydrophobic surfaces when the binding agents have been deposited at the points of

contact of the grains. This argument is in agreement with the observation on the adhesion of binding agent on hydrophobic chromite surface created by the contamination with grease as discussed in section 6.4.

On firing the pellets to 1000°C, a gradual increase in pellet strength was observed (see Table 17). This increase in strength could be attributed to the onset of sintering of solid resulting in an improvement in pellet strength. However, this could only proceed at points of contact of the ore particles. Where graphite particles separate the ore grains, sintering is initially prevented, and the compressive strengths of such pellets fired to under 1000°C is expected to be lower than that of pellets without graphite addition. For example pellets containing no graphite possessed a compressive strength of 9.2 kg. when fired to 1000°C but pellets containing 4% graphite and fired to the same temperature only had a compressive strength of 6.5 kg. At temperatures above 1000°C an increase in pellet strength was observed with an increase in graphite addition (see Table 17).

A study of polished sections of hard fired pellets revealed that at temperatures of 1200°C or over reduction by graphite leads to the formation of metallic iron (appearing white in photograph) commonly observed at the grain surfaces binding adjacent particles together as shown in the photograph of a polished section in Plate 2(A and B). The amount of metallic iron

present depends on the amount of graphite available for selective reduction, and consequently the more highly reduced pellets will have more iron bridges which may provide a higher compressive strength. An increase in compressive strength obtained by reduction-sintering of briquettes at 1340°C was also observed. The compressive strength was found to increase with increasing graphite (see runs 1, 2, 3 and 4, Table 16).

Sintering of Chromite at temperatures in excess of 1000°C.

Study of polished sections (Plates 2A and 2B) and microradiographs (Plate 3A and 3B) shows that the sintering of chromite pellets at high temperatures is caused by:

(1) Cementation of particles by metallic iron bridges

(2) Diffusional bonding between chromite grains

(3) Diffusional bonding between gangue minerals consisting mainly of serpentine

(4) Bonding by glassy matrix as a result of softening and resolidification of gangue minerals.

Sintering of chromite ore can be observed at a low temperature of 1340°C. Under reducing conditions, metallic iron bridges were formed cementing

(a) chromite particles to chromite particles

(b) gangue particles to gangue particles

and

(c) gangue particles to chromite particles. (See Plate 2A). This type of bridge (appear as white areas in the Plate)

commonly occur individually but occasionally they were reinforced by adjacent bridges of chromite (appear as grey areas in the Plate) or gangue material (not visible in the Plate). They were distributed evenly throughout the pellet indicating uniform reduction at high temperatures.

Plates 2A and 3A also show bridging of chromite grains by diffusion at points of contact at a sintering temperature of 1340°C. This type of bonding was, however, not very extensive, and the original chromite grain could still be observed to retain their granular outline showing no sign of complete recrystallisation or alteration into secondary minerals. Although the gangue was not shown in Plates 2A and 3A, microscopic examination revealed that the welding of gangue particles to one another and adhesion of gangue to adjacent chromite grains occur more extensively. The grains of the gangue appeared less angular and acquired a smoother outline than the chromite particles.

At temperature of firing of 1500°C, bridging by diffusion of solids became more extensive (see Plates 2B and 3B). The neck of the joint between two particles generally became thicker often resulting in the coalescence of smaller grains to form one larger particle. The extensive development of welding of particles frequently caused iron globules in the pellets to be trapped by adjacent chromite or gangue material. The iron deposited within the chromite grains was

found to be completely or partially enclosed by constriction or sealing of the openings to the cracks or channels in the grains. As a result of this, the chromite grains assumed a smoother outline than at 1340°C (see Plates 2B and 3B).

In addition to the above mechanisms of high temperature bonding, microscopic study of polished sections showed that diffusional bonding of gangue minerals still occurred at 1500°C, but, in addition, the formation of a glassy matrix with crystalline chromite and round metallic iron globules embedded in it was commonly found. This glassy matrix was probably derived from the melting and resolidification of some of the gangue minerals in the agglomerates. However, no secondary crystals were observed to have derived from the resolidification of the gangue and no dissolution of iron into the gangue or glassy matrix was detected.

On the contrary, complete recrystallisation of chromite grains could be observed at this temperature of sintering. Plate 4 shows a typical chromite grain which had recrystallised after firing to 1500°C under reducing conditions. A concentric zoned structure with various metal contents could be seen in the recrystallised "chromite", but the nature and composition of the material in the various zones had not been established. The extensive occurrence of the mechanism of diffusion, recrystallisation, and melting and resolidification in the pellets at 1500°C resulted in pellets having a denser structure (compare Plates 2A and 2B, 3A and 3B). The pellets

were found to have shrunk by about 10% in volume after firing to 1500°C.

6.6 Methods of Sintering.

Horizontal travelling grates and vertical shaft furnaces are at present the most widely used industrial appliances for sintering. For sintering and pelletizing of iron ores, horizontal Dwight-Lloyd type travelling grate machines are commonly employed with firing techniques including updraft, downdraft or a combination of both. Violetta (53) discussed the advantages of updraft firing on a horizontal grate, while downdraft firing was advocated by English and Morgan (54). Kurt, Meyer and Rausch (55), however, suggested using a travelling grate combining the techniques of downdraft burning and drying, and updraft cooling. All these practices, however, share the disadvantage of being unsuitable for efficient atmospheric control during firing and cooling which is essential for reduction during the sintering of chromite pellets. The acid-soluble iron must not be reoxidised (13) during the period of cooling and to this effect, sintering in a vertical shaft furnace is more suitable. This process of sintering can only be applied to lumpy material to ensure adequate gas passage through the vertical column of charge which may be up to 20 ft. in height. The principle of counter-flow in this operation facilitates efficient heat recovery from all outgoing materials. A major drawback lies

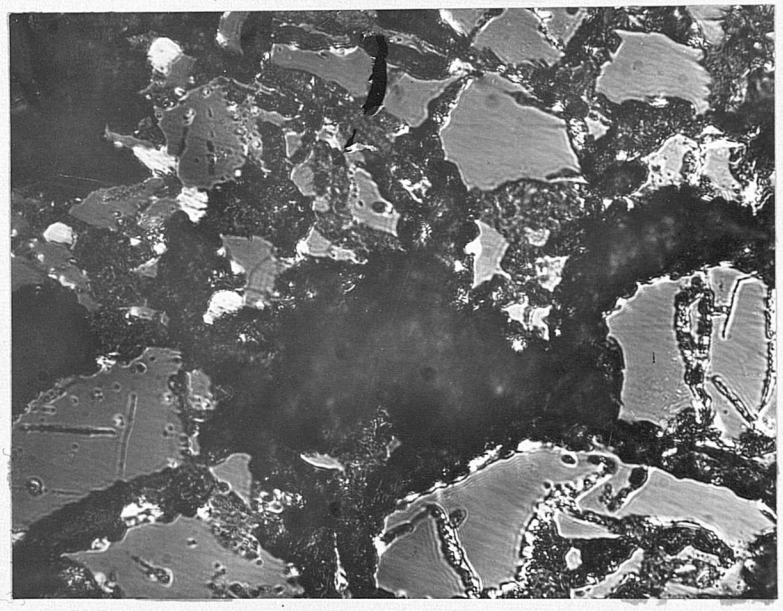


PLATE 2A. Polished Section of Chromite Agglomerate Reduced at 1340°C.
(×570)

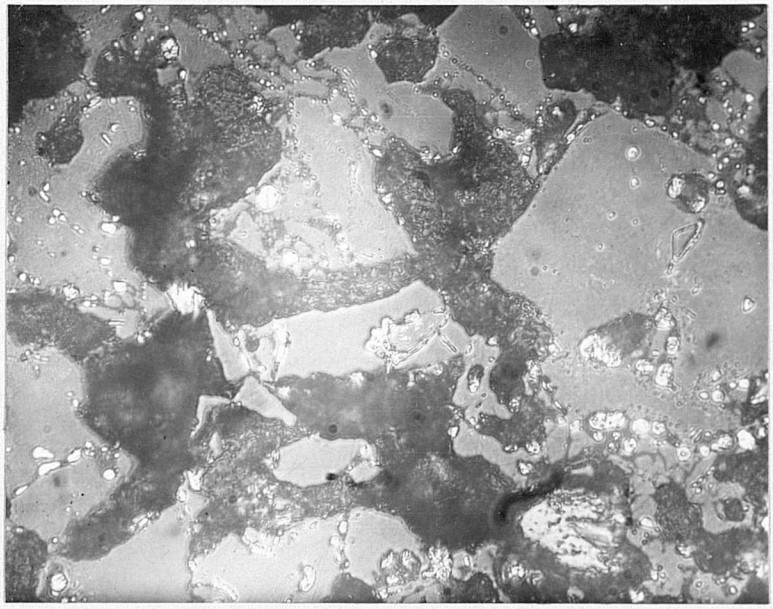


PLATE 2B. Polished Section of Chromite Agglomerate Reduced at 1500°C.
(×570)

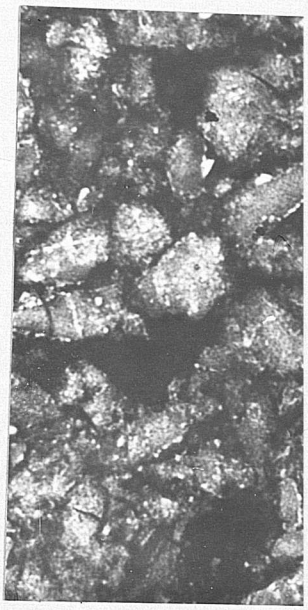


PLATE 3A. Microradio
Red



hromite Briquette
40°C.
(×190)

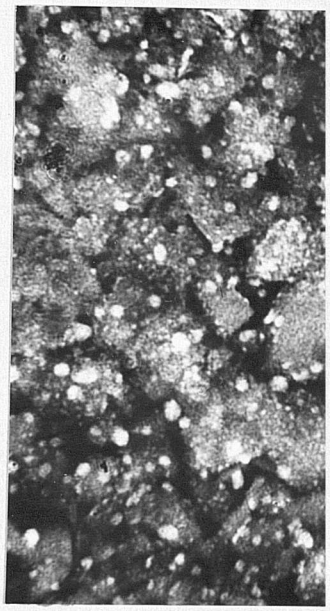
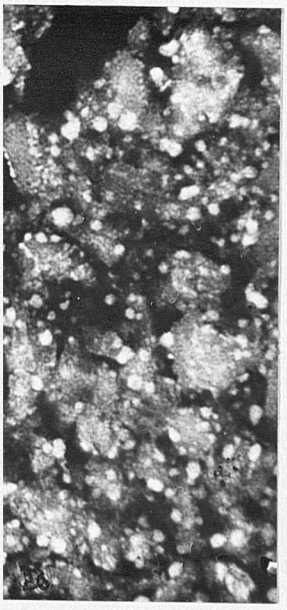


PLATE 3B. Microradiog
Redu



romite Briquette
0°C.
(×190)

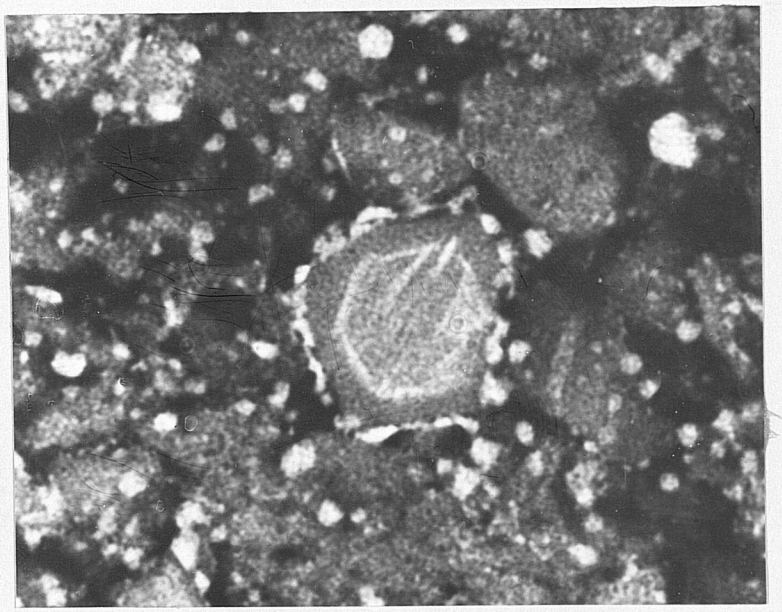


PLATE 4.

Microradiograph of Recrystallised "Chromite".

(x340)

in the difficulty of maintaining a uniform hot zone across the furnace so that no part of the charge is either over-fired or under-fired.

Amongst the various types of vertical kilns, the plain cylindrical or rectangular shafts with external annular combustion chambers are the most popular in established pelletizing practice. Cylindrical designs range in size up to six feet in diameter (48) but for furnaces of larger capacity, shafts of rectangular cross-sections are employed, because they offer a better cross-sectional temperature distribution (59). Oil is the fuel most commonly employed and heat from exothermic reactions is sometimes utilised, e.g. in firing magnetite pellets under oxidising conditions.

With an external combustion-chamber, only the combustion-products are used forheating the furnace burden. If combustion of the fuel could be conducted internally, in the interstitial spaces of the furnace burden, heat losses from the combustion chamber would be avoided. A small vertical shaft furnace was, therefore, constructed for this workin order to investigate the possibility of internal combustion of town gas in the interstitial spaces of the burden.

6.7 The Furnace

The furnace consisted of a vertical refractory stack 2' 6" high, with a circular cross section, tapering from 7"

internal diameter at the bottom to 4" internal diameter at the top. The stack wall was 3" thick and was constructed of five annular sections cast in Morgan Castable refractory which may be operated at temperatures up to 1650°C. The stack was supported on a metal stand and was shielded by a cylindrical metal sheath of 18" diameter. The annular space between this shield and the refractory stack was filled with Stillite Wool for insulation (see Fig.21). In good firing practice, the stock line should be maintained at a constant level at the top of the furnace. This was to avoid damaging the pellets through physical and thermal shock and to attain a good heat recovery from the waste gases. To this effect, it was arranged to supply green pellets to the furnace via an adjustable launder from a small feed hopper supported above the furnace (see Fig.22). Pellets from the hopper discharged by gravity along the launder into the stack. Gravity flow of the pellets stopped once the stack was full but when the level in the stack fell, more pellets would roll in to maintain the stock line. The rate of throughput of the furnace and the level of pellets in the hopper had no effect on this feeding device. Fines produced in the feed hopper were removed by means of a perforated section in the launder to prevent their entry into the furnace where they could cause blockage to air flow.

Another pre-requisite of consistent firing is a steady rate of descent of the pellets through the stack. A discharge mechanism was, therefore, fitted at the bottom of

SKETCH OF SHAFT FURNACE

FIG 21

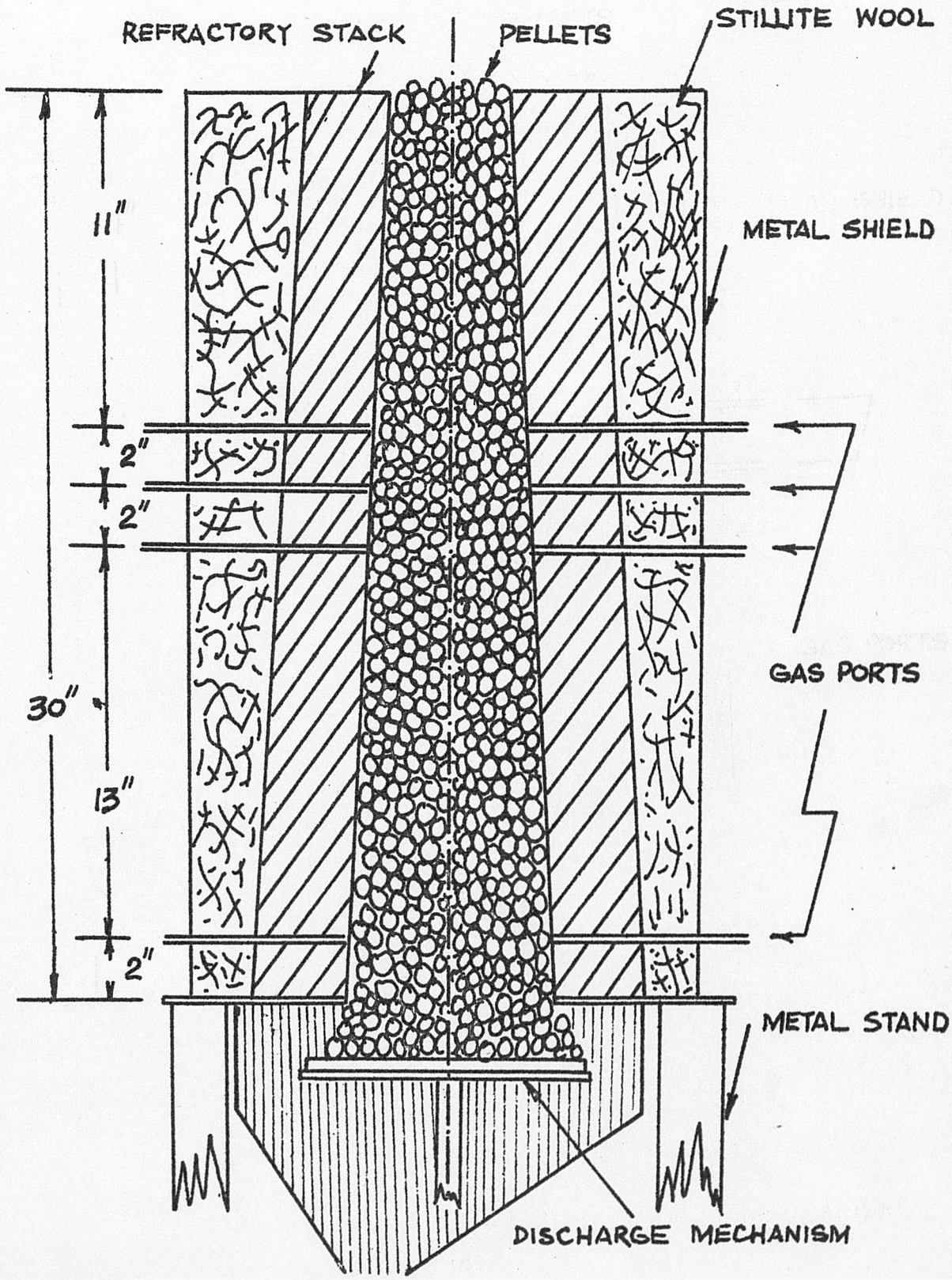
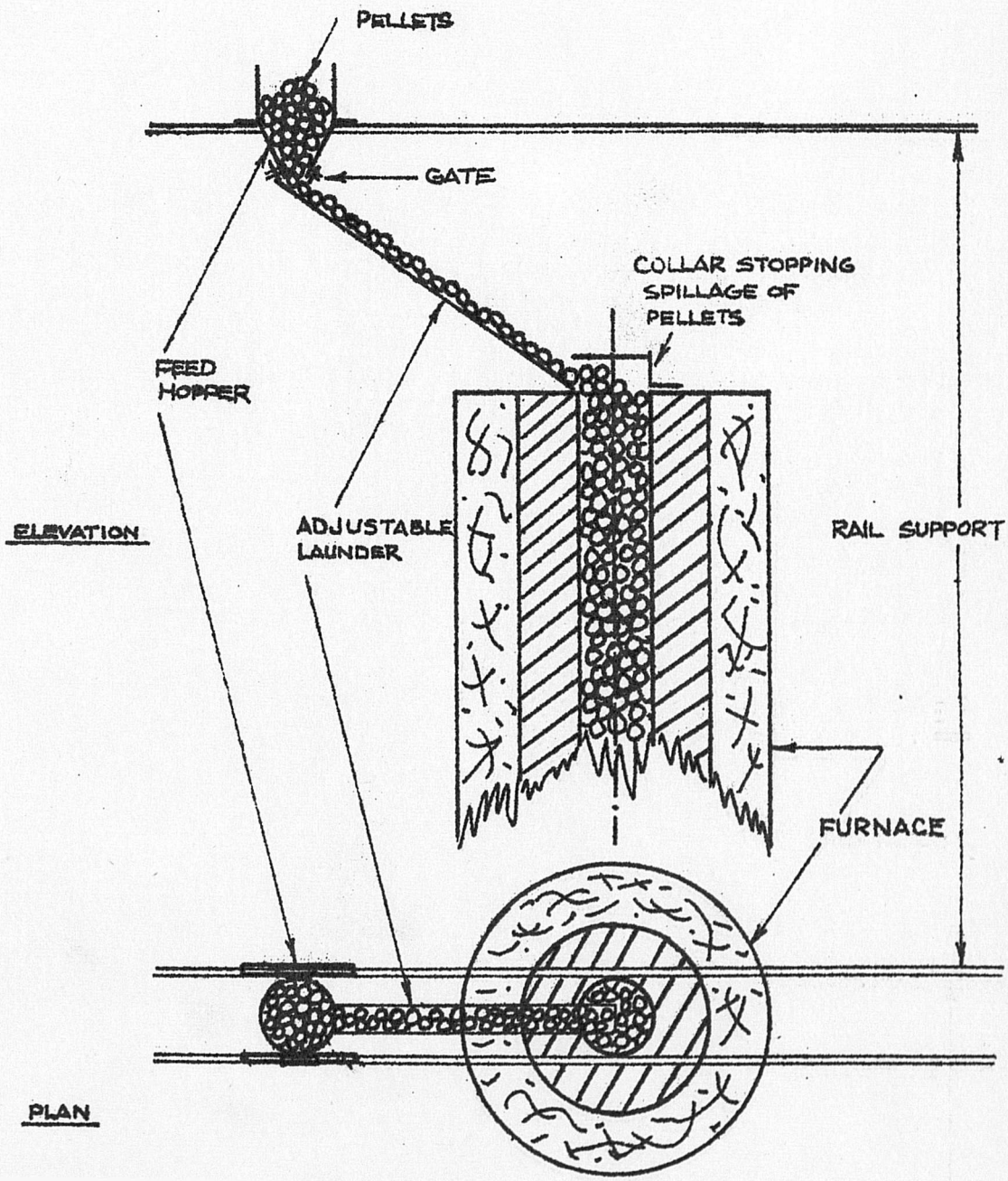


FIG 22

FEED ARRANGEMENT OF THE FURNACE

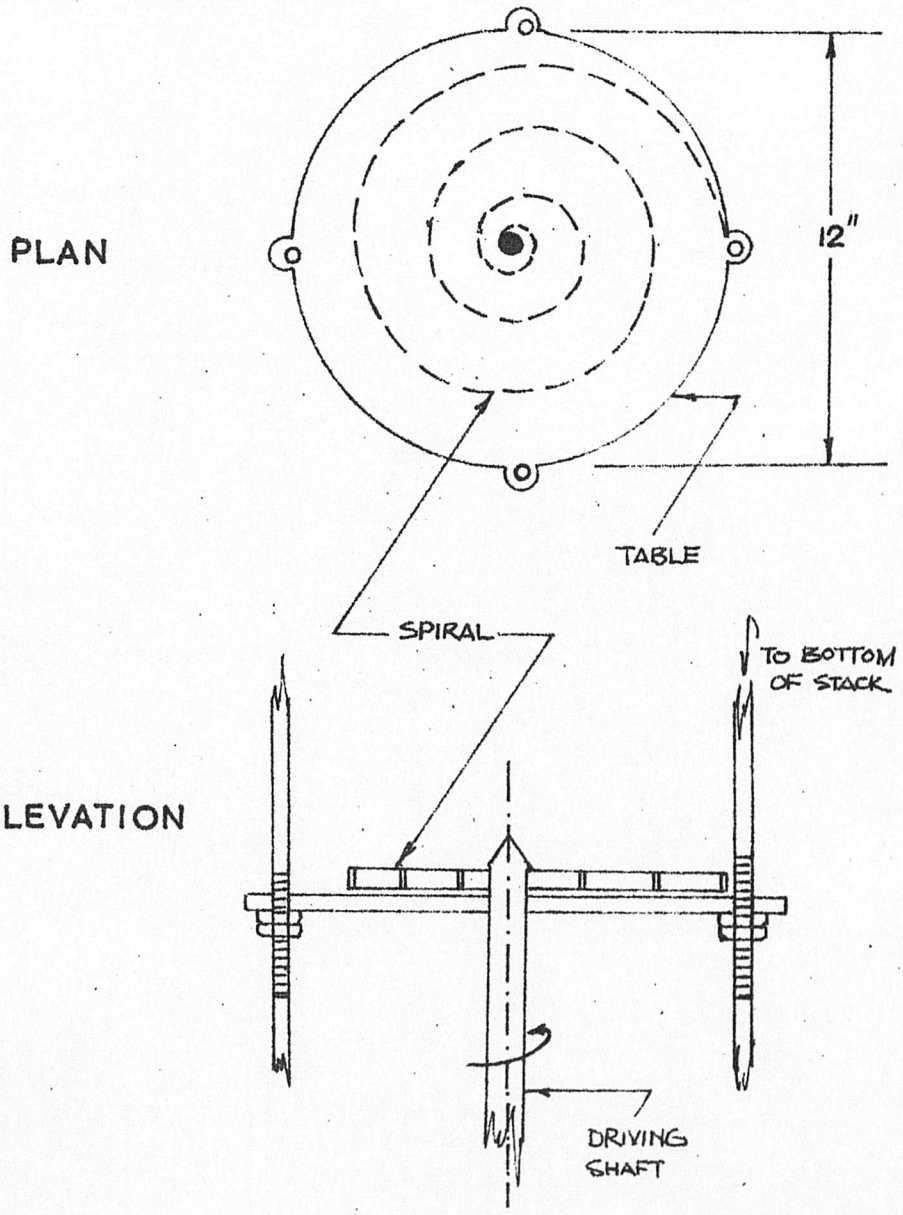


the furnace. In its initial version, the mechanism consisted of a circular metal table supporting the pellets in the stack and of a peripheral scraper with a motor and ratchet drive. The scraper was intended to remove a few pellets at a time, but it was found that discharge was irregular. A stationary load accumulated over the centre of the table and unstable conditions occurred from time to time, resulting in the rapid escape of a large part of the furnace charge.

The discharge table was therefore redesigned. The peripheral scraper was replaced by a rotary spiral cutter which started at the centre of the table and extended to the edge in two 360° turns (see Fig.23). Rotation of this spiral blade by a motor and ratchet device caused continuous outward displacement of pellets from the centre, and at the same time the presence of the blade prevented any avalanching of the charge. This method of pellet removal from the centre resulted in a constant rate of vertical descent in the stack. Adjustments of the speed of rotation of the spiral and of the clearance between the stack and the table provided a choice of constant rates of vertical descent in the stack from 0.2"/min. upwards, with $-\frac{3}{4}"$ $+\frac{1}{2}"$ pellets. Pellets which were discharged over the edge of the table fell into a sealed hopper which completely enclosed the discharge mechanism. Pellets could then be periodically removed from the hopper or they could be discharged continuously into a tank filled with water or

FIG 23

SPIRAL DISCHARGE MECHANISM



leaching solution.

Gas and air for combustion could be fed to the shaft through 16 ports arranged in groups of four at 11, 13, 15 and 28 inches from the top of the stack (see Fig.21). Each group of four ports was supplied from independently controllable ring main bustle pipes and the flow to each port could be adjusted individually through altering the internal diameter of the gas ports by means of annular inserts of mullite tube. This raises the gas velocity and depth of gas penetration into the charge at any given rate of gas feed, and permitted adjustments of the temperature distribution across the stack.

The range of gas port levels facilitated siting of the zone of combustion at different heights in the stack. It also permitted good control of the atmosphere during cooling of the burden. For cooling under oxidizing conditions, air was introduced near the bottom of the stack while for cooling under a neutral atmosphere, this could be replaced by nitrogen or carbon dioxide. The air was supplied from the compressed air main through a pressure-reducing valve; the combustion-gas was taken from the town gas main.

The supplies of air and gas to the furnace were measured by means of rotameters mounted on a controlling panel which also housed a Honeywell 6-point temperature recorder and a Honeywell proportional temperature indicator/controller. Temperatures were

measured by means of 15 platinum/platinum rhodium thermocouples shielded by mullite tubes embedded radially at different levels in the wall of the stack. It was found necessary to have the thermocouples protruding at least ½" into the stack to avoid excessive masking of temperature changes by wall effects. The temperature at the centre and side of the shaft was also measured by means of two vertical thermocouples which could be raised or lowered inside mullite sheaths, suspended vertically in the stack. The thermocouples and those embedded in the refractory wall could be connected through a selector switch to the controller, or to the recorder so that any combination of six temperatures could be recorded and a seventh used for controlling the air/gas flow to the furnace. The selector switches further permitted instantaneous reading of any of the remaining thermocouple and it was possible to explore the temperature distribution in the furnace under different types of firing conditions.

6.8 Firing Conditions.

To facilitate preliminary firing runs without pellets or with only small batches of material, a "permanent" inert furnace charge in the form of ½" alumina pellets was prepared. These could be circulated through the furnace during adjustment of firing conditions and exploration of temperature distribution at various zones in the furnace. The alumina pellets were also

used at the completion of every run to maintain a full stack while the last of ore pellets were being fired and discharged.

10% water was added to the alumina pellets for preliminary studies of the location and geometry of temperature zones in the furnace; different combinations and methods of gas and air flows were used.

In order to effect efficient preheating of the air employed for combustion, it was introduced at the bottom of the stack, so that, on rising, it was heated by the descending burden. Town gas was fed to the furnace through gas ports 11" from the top. It was discovered that the temperature distribution was very irregular, owing to poor gas penetration into the centre of the stack. Four isolated small hot zones occurred at gas velocities of 5 ft./sec. in restricted areas immediately surrounding the gas ports as shown in Fig. 24. At higher gas feed rates (8 ft./sec.) the zones expanded, merged, and ultimately rose nearly to the top of the stack, where an excessively steep temperature gradient was resulted, but the gas inlet velocity remained insufficient to cause penetration into the centre of the stack (see Fig.25). An increase in the air supply only succeeded in raising the hot zone to the top of the furnace. The hot zone was at best of dome shape, supported by four "legs" rising from the gas ports. Changes in the rate of burden descent had little effect on the geometry and location of the hot zone.

This condition was remedied by using gas feed pipes of smaller diameters. This increased the gas inlet velocities and provided adequate gas penetration to the centre of the stack. A reasonably uniform hot zone was produced at approximately ½" above the gas ports and extended upwards for a distance of about 6" (see Fig. 26). With the temperature in the hot zone at 1300°C the corresponding temperature at the top of the stack was in the region of 150-200°C, sufficient to prevent condensation of steam at the top of the charge.

The hot zone could be moved towards the top of the stack by reducing the rate of descent of the charge or by increasing the volume of air supply. Conversely, the hot zone could be pulled further down the stack by increasing the rate of descent or decreasing the air flow.

Differences in temperatures between the centre and the sides of the stack could be avoided only by very careful regulation of the inlet gas velocity. Any sudden decrease in gas inlet velocity resulted in a cooler centre while a sudden increase in the gas feed velocity produced the opposite effect. It was, therefore, difficult to control the maximum temperature in the hot zone by altering the gas and air feed rates without adjusting the gas inlet velocity. For automatic control it was found most convenient to adjust the rate of throughput in the furnace so as to maintain a constant hot zone with even temperature distribution.

FIG 24

TEMPERATURE DISTRIBUTION IN FURNACE WHEN GAS VELOCITY WAS LOW

TOWN GAS	9 l/MIN	RATE OF DESCENT	0.6"/MIN
AIR	65 l/MIN	MOISTURE IN FEED	9 %
GAS : AIR	1 : 7.2	TOWN GAS VELOCITY	5'/SEC

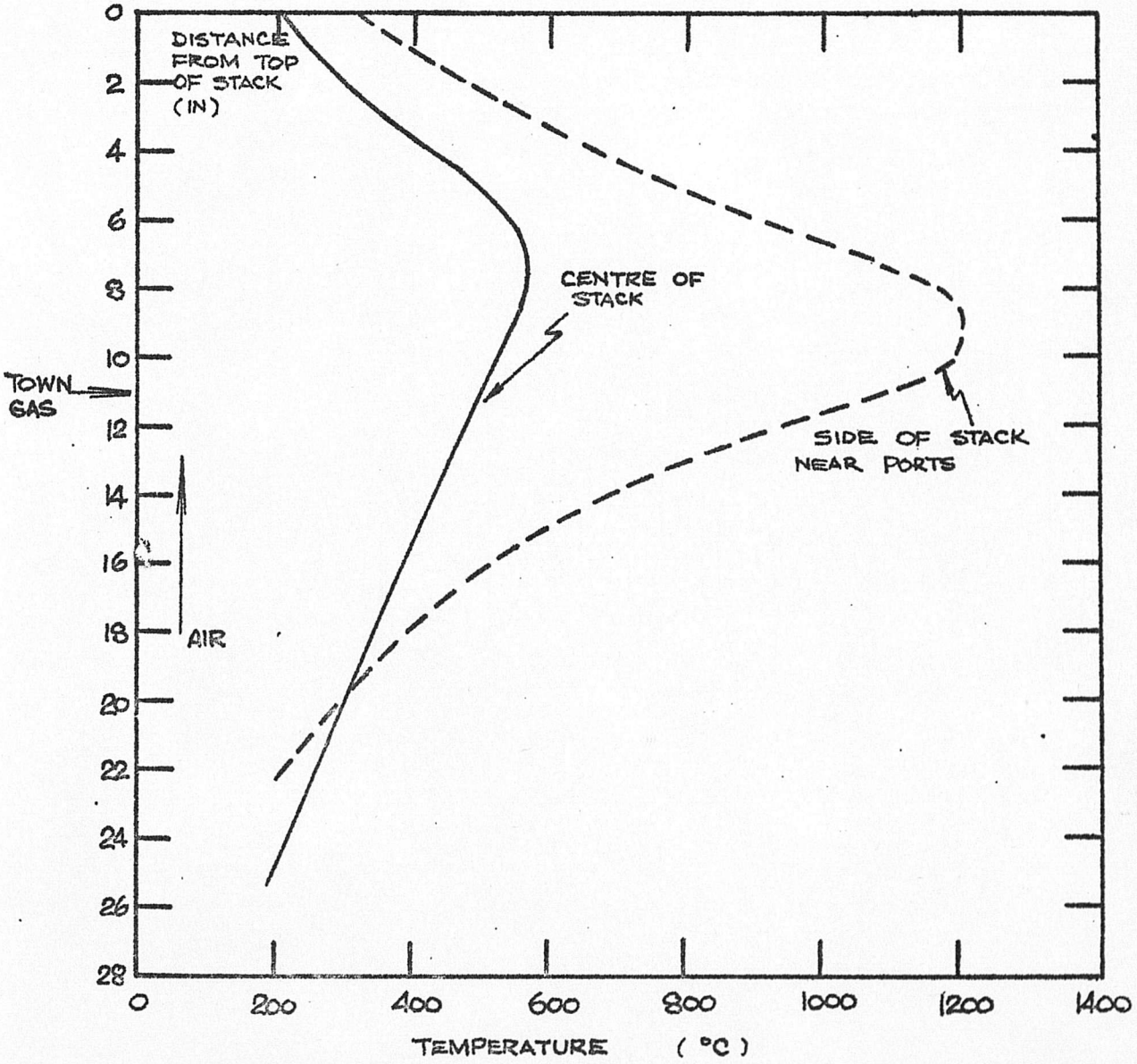


FIG 25

TEMPERATURE DISTRIBUTION IN FURNACE WHEN GAS VELOCITY WAS SLIGHTLY RAISED

TOWN GAS —— 14 ℓ/MIN
AIR —— 140 ℓ/MIN
GAS : AIR —— 1 : 10·0

RATE OF DESCENT —— 0·6"/MIN
MOISTURE IN FEED —— 9 %
TOWN GAS VELOCITY —— 8'/SEC

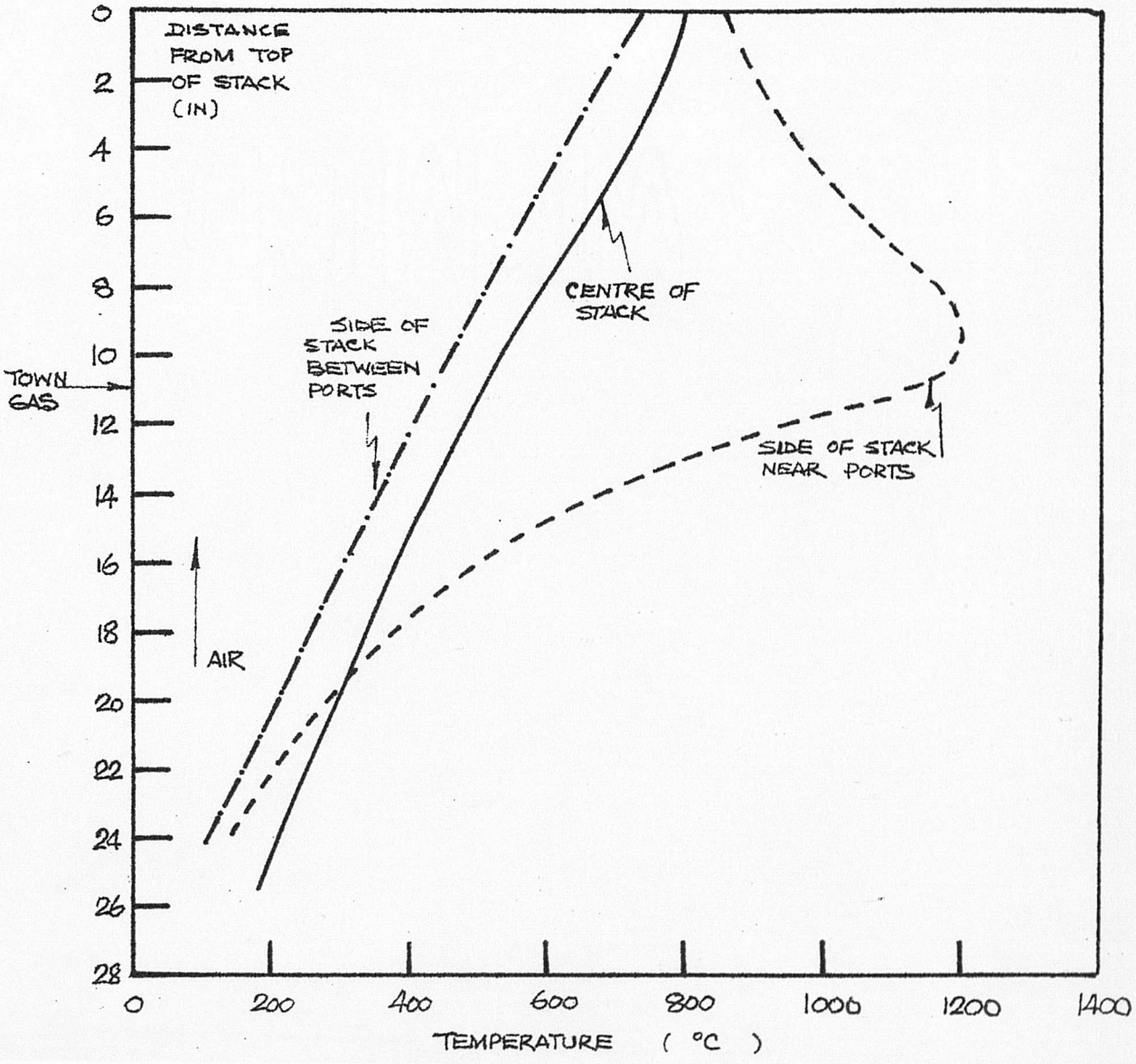
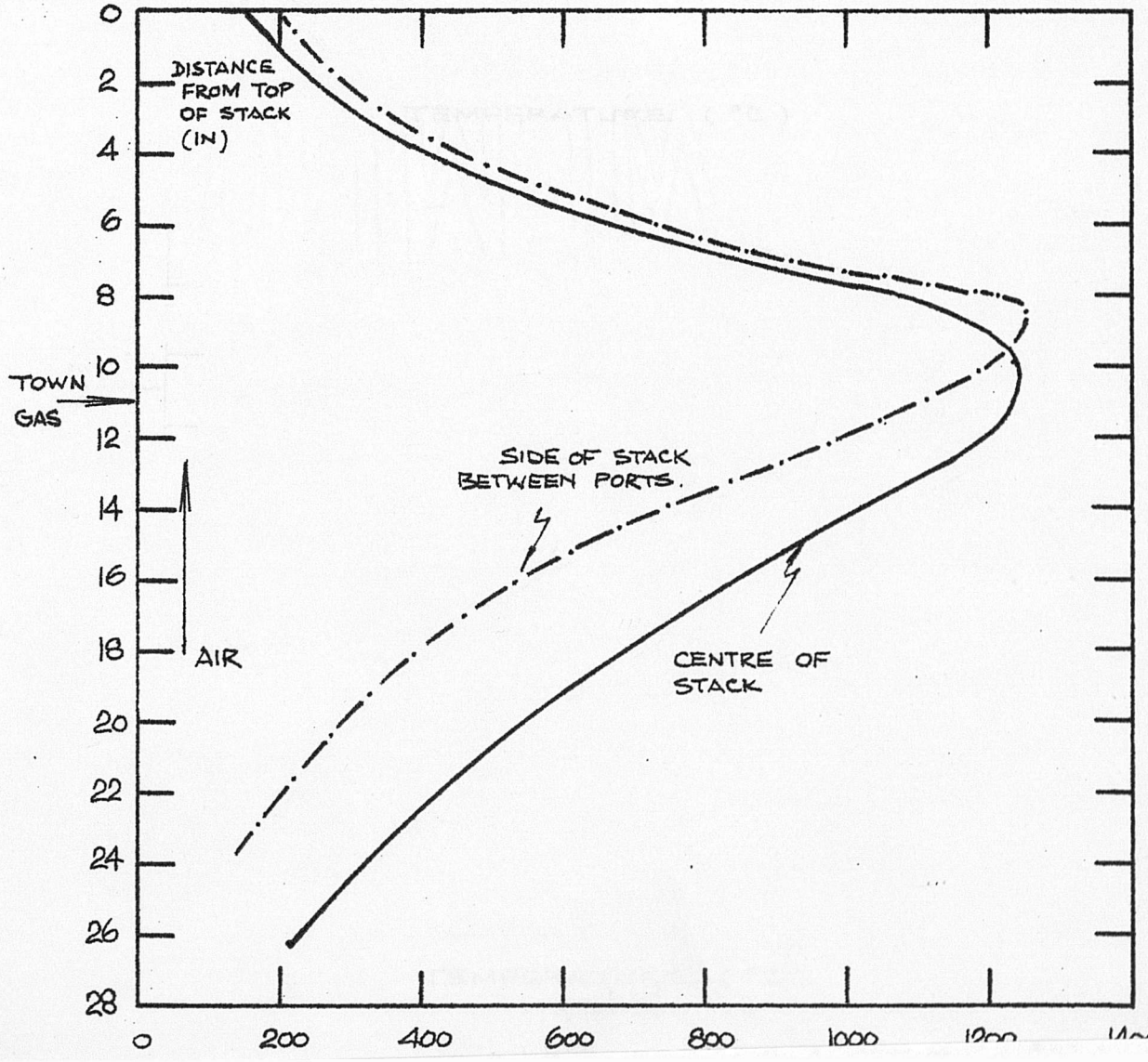


FIG 26

TEMPERATURE DISTRIBUTION IN FURNACE WHEN GAS VELOCITY WAS HIGH

TOWN GAS	9 ℓ / MIN	RATE OF DESCENT	0·6″/MIN
AIR	65 ℓ / MIN	MOISTURE IN FEED	9 %
GAS : AIR	1 : 7·2	TOWN GAS VELOCITY	25′/SEC



Preliminary tests had shown that manganese dioxide pellets disintegrated badly when fired in a crucible furnace under an atmosphere of town gas, but no breakage occurred under neutral or oxidizing conditions. Manganese dioxide pellets were, therefore, used to explore further the atmospheric conditions in the hot zone of the shaft furnace. It was found that only part of the pellets disintegrated in passing through the shaft furnace, and this was accepted as proof that localised oxidizing regions existed in the hot zone.

In reducing and sintering chromite pellets the hot zone must be entirely reducing and an oxidizing atmosphere is undesirable even in the cooling section of the furnace.

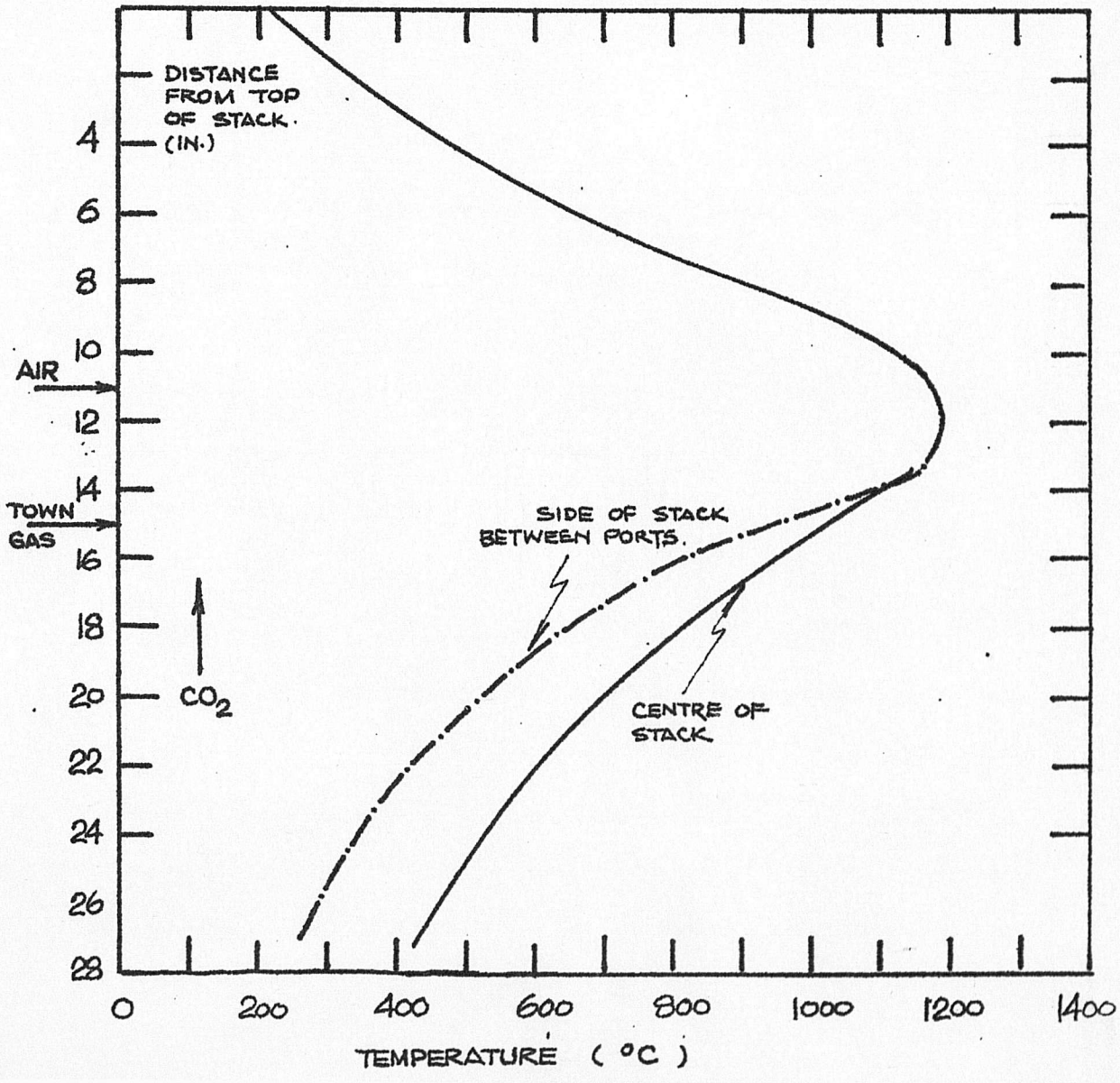
Firing procedure was therefore changed so that air was admitted through ports 11" from the top of the furnace and town gas through ports situated 4" below. A stream of carbon dioxide or nitrogen was introduced through the lowest set of gas ports so as to act as a medium for heat recovery and to prevent any accumulation of town gas at the bottom of the stack. This mode of operation produced a hot zone 4-5" deep, at the level of the air inlet ports. The temperature was uniformly distributed (see Fig. 27) and firing of manganese dioxide pellets indicated that the atmosphere of the hot zone was completely reducing even at a gas to air ratio of over 1:5. With this set-up, it

FIG 27

TEMPERATURE DISTRIBUTION IN FURNACE WITH CO_2 FOR HEAT RECOVERY

TOWN GAS —— 25 ℓ / MIN
AIR —— 100 ℓ / MIN
GAS : AIR —— 1:4
CO_2 —— 40 ℓ / MIN

RATE OF DESCENT —— 0·7"/MIN
MOISTURE IN FEED —— 0 %
TOWN GAS VELOCITY —— 27'/SEC.



appeared that the gas-carbon dioxide or gas-nitrogen mixtures ignited in an atmosphere of air in the interstitial spaces in the burden and the atmosphere immediately below the hot zone could thus be only reducing.

This arrangement, however, failed to provide adequate preheating of the air and the temperature in the hot zone could not be raised above 1200°C as compared with 1400°C obtained previously. In addition the fuel consumption for the same rate of furnace throughput rose to twice the previous quantity required to maintain a hot zone with higher temperatures. Nevertheless, the furnace was used to sinter ½" chromite pellets with a 5% sodium chloride solution as binder and 4% graphite as reducing agent. The pellets survived the rapid drying and preheating stages in the furnace without breakage. Extensive exfoliation of the pellet was again observed in the firing zone. The products were very brittle and unsuitable for further processing.

Chromite pellets also exfoliated extensively when fired in a crucible furnace under an atmosphere of town gas although firing under neutral or oxidizing atmospheres produced no disintegration. On the contrary, the pellets were actually found to be stronger (see Table 18). Hence the exfoliation and disintegration of the chromite pellets in the hot zone of the shaft furnace could be attributed to the atmosphere of town gas.

TABLE 18

Compressive Strength of Pellets Fired to 1200°C in Crucible Furnace Under Various Conditions.

Condition of Firing	Strength of Pellets (Kg)	Remarks
Oxidizing with air	18.8	Pellets bluish, slightly magnetic
Reducing with 2% C.	17.5	Pellets bluish, magnetic.
Reducing with 4% C.	17.3	Pellets bluish, highly magnetic
Reducing with town gas	9.1	Pellet brown, exfoliated, magnetic

Although this method of firing yielded a uniform reducing hot zone, it remained unsuitable for the sintering of chromite pellets. Solid fuel firing offered an appropriate alternative but in view of the endothermic nature of selective reduction of chromite by graphite (see Table 19) (18), an excessive amount of graphite would have had to be incorporated in the burden as fuel. The amount of air for combustion of this excess graphite would require careful control and this would present considerable practical problems.

It was concluded that, firing of chromite pellets in a shaft furnace had to be conducted by the conventional method of heating the burden with combustion products from an external annular combustion chamber. The atmosphere in the combustion chamber should be neutral for efficiency in the reduction

process, and to avoid any reoxidization or exfoliation of pellets.

TABLE 19

Heats of Reaction (cals/mole)

of 1. $FeO.Cr_2O_3 + C = Fe$ (α, γ or δ) $+ Cr_2O_3 + CO$

2. $FeO.Cr_2O_3 + C = Fe$ (γ) $+ Cr_2O_3 + CO$

3. $FeO.Cr_2O_3 + \frac{4}{3} C = \frac{1}{3} Fe_3C$ (β) $+ Cr_2O_3 + CO$

T^oK	T^oC	ΔH_1	ΔH_2	ΔH_3
1100	827	46400	-	47500
1200	927	46300	46600	47200
1300	1027	46100	46300	46900
1400	1127	45900	46000	46500
1500	1227	45700	45700	46100
1600	1327	45400	45300	45700
1700	1427	45100	-	45200

7.0 REDUCTION AND LEACHING

7.1 Introduction.

The presence of carbon during the sintering of chromite pellets leads to the selective reduction of iron oxide to metallic iron. The latter is acid-soluble and can be removed by leaching, thus leaving a residue with a higher chromium:iron ratio.

The selective reduction of chromite commences at a temperature of 1027°C (18). At this temperature the standard free energy of the reduction reaction is high (see Table 3) and the reaction can proceed to completion only with difficulty. However, if the temperature is increased to 1200°C, the reduction of trivalent chromium will also occur (see Fig. 1). It seems preferable, therefore, to conduct the reduction of chromite at a temperature below 1200°C. Strong pellets, however, cannot be produced at such a low temperature of sintering. A compromise at a higher firing temperature is necessary and the production of a small amount of acid-soluble chromium must be tolerated.

It is possible to avoid undue formation of acid-soluble chromium because the divalent iron is more readily reduced than the trivalent chromium. If no excess carbon is present beyond the requirements for iron oxide reduction, the available carbon is rapidly consumed before reduction of chromic oxide becomes widespread.

The optimum quantity of reducing agent for this purpose

cannot be established theoretically owing to complications by side reactions leading to the formation of carbides of iron (18). In the case of chromium, Boericke (64) reported the existence of various carbides, the most common being Cr_4C, Cr_7C_3 and Cr_3C_2. These carbides are stable but can act as reducing agents, producing metallic iron, chromium and carbon monoxide.

The reduction process may be further complicated by the presence of small amounts of foreign ions in the pellets, affecting high temperature chemical reactions. For example, it has been reported that partial or total chlorination of chromite can take place under reducing conditions in the presence of chloride ions (12) (65). The rate of reduction of chromite by hydrogen or graphite to iron, Cr_2O_3 and H_2O or CO is stated to be strongly accelerated by the addition of 3% K_2CO_3 (62). In the reduction of chromite pellets, the presence of foreign material cannot be readily excluded and some are deliberately incorporated in the pellets in the form of binding agents. It is necessary to ensure, therefore, that gangue and any added substances have no adverse effects on reduction-roasting which must render iron acid-soluble and on the subsequent leaching process which must remove iron without excessive solution of chromium. The problem involves accessibility as well as solubility on the metal.

7.2 Quality Control.

For the purpose of determining the amount of acid-soluble metals produced by the reduction process, pellets were leached with acid under controlled conditions. To this effect, the amounts of acid employed were ten times in excess of the estimated quantity required on stoichiometric considerations, and the weight of pellets or briquettes leached per batch was not less than 15 grams. In any one series of experiments, the conditions of leaching were kept identical to ensure reproducibility and to enable comparison.

A conventional method for the analysis of iron and chromium in the mineral requires initial alkaline fusion of the finely ground solid (see Appendix I). This procedure is necessarily long and cumbersome, and was considered impractical for the large number of determinations in this work. This method was used from time to time for checking the results obtained by means of a speedier indirect method of iron and chromium determination.

This indirect method of analysis relies on the determination of iron and chromium in the leach liquor extracted from a known weight of material. The grade of the final product and the chromium:iron ratio could thus be deduced from the values of the head assay.

The iron and chromium content of the leach liquor may be determined by conventional titrimetric methods which are

comparatively simple but slow in manipulation. A rapid spectrophotometric method of analysis was, therefore, developed (see Appendix 2) based on the formation of stable ferric-EDTA and chromic-EDTA colour complexes at pH 1.5 - pH 4.0 (see Appendix 2). The optical density of the chromic-EDTA complex was measured at a wavelength of 548 mμ and that of the ferric-EDTA complex at 329.5 mμ. The colours of the two complexes do not interfere, and separation is, therefore, not required. Solutions containing 2 to 20 mg ferric ion per litre can be measured using 1 cm absorptiometric glass cells, and in the determination of chromium, sensitivity is between 20-200 mg of chromium per litre of solution.

Two methods of microscopy were used for determining the location of acid-soluble iron and for studying other textural and structural changes in the pellets or briquettes: (a) the study of microradiographs of thin sections and (b) the study of polished sections of the specimens.

X-ray diffraction photographs of powdered samples were also taken before and after treatment to ascertain whether crystals in the reduced and leached products retained the structure of the chromite spinel. For this purpose, a cobalt target with an iron filter was used at 45 K.V. and 6 m.A. The diffraction photographs were compared to observe any loss, addition or displacement of lines which would be indicative of the destruction or change of existing crystals or of the formation of new crystalline phases.

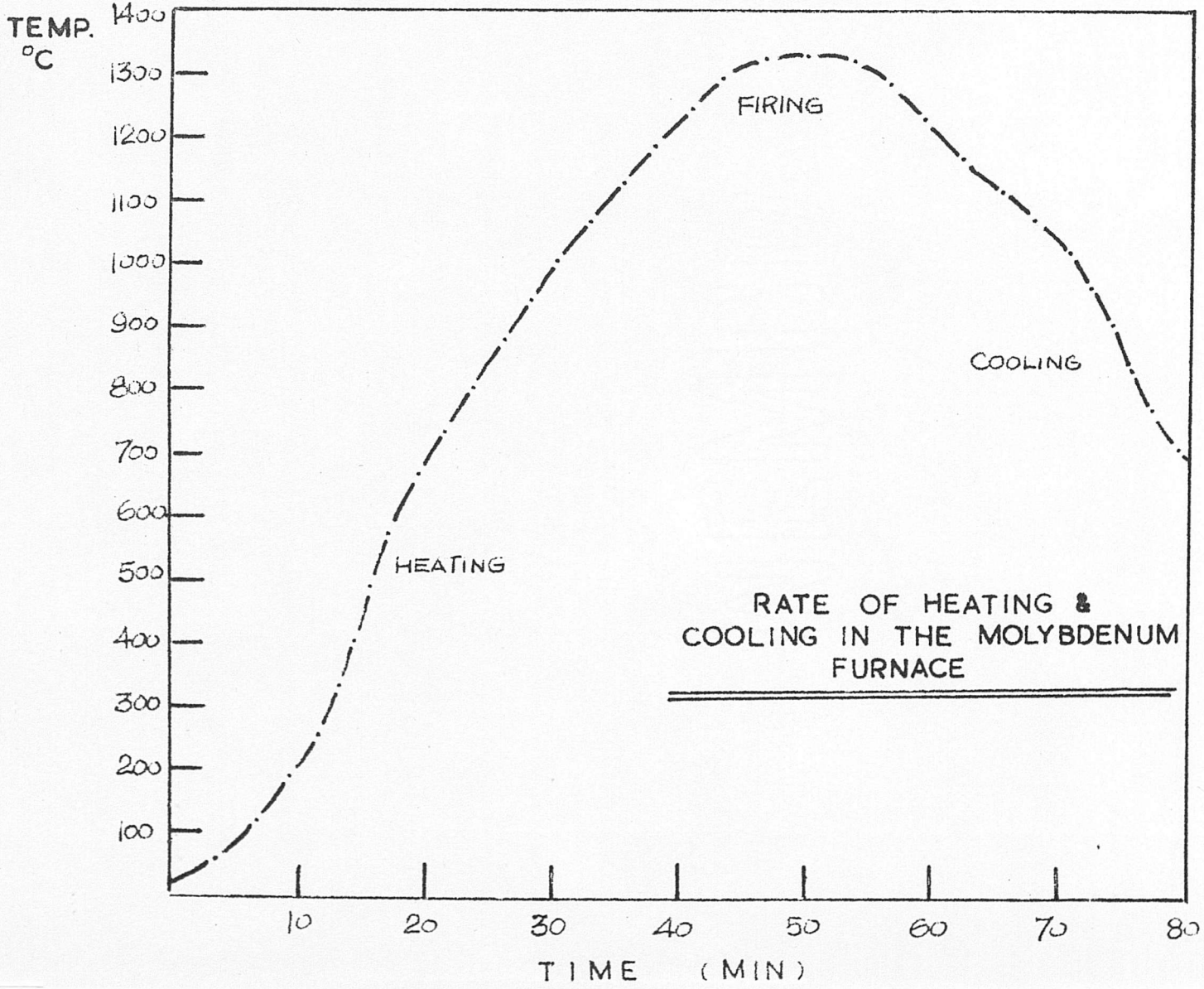
7.3 The Effect of Binding Agents on the Removal of Acid-Soluble Iron and Chromium.

The effect of various binding agents on the extraction of iron and chromium from the reduced chromite was investigated. For this purpose, $\frac{1}{2}$" diameter x $\frac{1}{3}$" thick briquettes of 5.0 g. each were used. After addition of the binder and an appropriate amount of finely ground graphite, the mixture was briquetted in a Millen Mounting Press at 4500 lb/sq.in. The briquettes were dried, fired and leached and the results were then assessed.

It was decided to investigate only the effects of those binders which had proved suitable for producing hard fired pellets. For the purpose of comparison, briquettes made with a mixture of bentonite and sodium carbonate solution were also included in the investigation.

Firing was conducted at various temperatures in a vertical molybdenum tube furnace of Kitchener and Bockris design (63). Shaft furnace conditions were simulated to some extent by operating the molybdenum tube furnace continuously with briquettes fed to the top of the vertical refractory tube and discharged from the bottom. The rate of descent was kept constant at 0.4"/min. The corresponding rates of heating and cooling are shown in Fig. 28. Reoxidation of the fired products was prevented by passing a gentle stream of forming gas containing 10% hydrogen and 90% nitrogen up the furnace. It was first established that this gas

FIG 28


TEMP. °C
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
FIRING
COOLING
HEATING
RATE OF HEATING & COOLING IN THE MOLYBDENUM FURNACE
10
20
30
40
50
60
70
80
TIME (MIN)

has a negligible effect on the reduction of chromite under the given conditions.

The fired pellets were discharged at about 200°C and were quenched directly in 10% sulphuric acid at room temperature (15°C). A standard leaching time of 2½ hours was maintained as a practical compromise although it was observed that leaching still proceeded slowly after this period.

After leaching, the liquor was separated from the residue and analysed for iron and chromium, using the spectrophotometric method (see Appendix 2). The results of this series of tests are shown in Table 20.

It may be seen that the binding agents had a significant effect on the amount of acid-soluble metals, some producing a larger yield of extractable metals than others. Sodium chloride gave the best results in this respect.

7.4 Effect of Temperature of Reduction on the Amount of Acid-Soluble Iron and Chromium.

Results of the above investigation indicated that the temperature of reduction can influence the amount of acid-soluble iron and chromium which appear to decrease with increasing temperature of sintering. A similar effect was observed by Downes and Morgan (7) at reduction temperatures above 1200°C, but no explanation was offered.

TABLE 20

Effects of Graphite Content, Firing Temperature, and Binding Agents on Acid Leaching of Chromite Briquettes

Firing Temp.	Binding Agent	% Extraction of Metal					
		1%C		2%C		4%C	
		Cr	Fe	Cr	Fe	Cr	Fe
1340°C	A	Negligible	14.0	Negligible	29.5	2.0	34.2
	B	"	17.3	"	18.7	0.5	23.9
	C	"	13.1	"	18.7	1.3	29.0
	D	"	8.4	"	20.1	1.3	29.0
1420°C	A	"	10.8	"	19.2	1.7	28.2
	B	"	10.3	"	16.4	1.3	29.7
	C	"	8.4	"	16.8	1.1	23.9
	D	"	10.3	"	15.5	1.7	22.9
1500°C	A	"	7.1	"	15.7	1.7	40.2
	B	"	8.4	"	15.1	1.1	22.9
	C	"	7.0	"	14.0	1.1	20.6
	D	"	6.5	"	13.5	1.1	20.1

Binding Agents A - 5% NaCl Soln.
B - 0.5% bentonite
C - 3% H_2SO_4 soln.
D - 0.5% bentonite + 5% Na_2CO_3 Soln.

Dwelling Time in Hot Zone - 7-10 min.
Conc. of Leach Liquor - 10% H_2SO_4
Temp. of Leach - quenching at 200°C then leached at 20°C
Time of Leach - 2½ hours.

It can be considered that at a sufficiently high temperature (e.g. 1340°C), all the carbon in the pellets rapidly oxidises or combines with the remaining solid until no free carbon is left. The temperature alone should have little effect on the amount of acid-soluble metal produced provided that the dwelling time is sufficiently long for the reaction to take place. However, the temperature of firing may increase the degree and extent of sintering, causing complete occlusion of metal drops in acid-resistant glassy or crystalline gangue or chromite. This will lower the apparent proportions of acid-soluble metal. Microscopic studies were therefore resumed to determine whether a distinction is needed between accessible and inaccessible metal.

The study of polished sections and microradiographs indicated that some of the metallic iron was situated at the surfaces of the grains as stringers, globules or bridges, while some was located in the internal cracks and channels inside individual grains or embedded in the glassy matrix. (See Plates 2A, 2B, 3A, 3B and 7). During the extraction of the metallic iron with sulphuric acid, easily accessible metal was rapidly removed, but the remaining iron situated inside the grains was less readily reached and might remain intact at the end of the leaching period (ref. section 7.12). It may be necessary, for example, for air or gases trapped inside cracks to be displaced before the acid can reach the metal. It is also necessary that the dissolved metal and any

gases produced during leaching should diffuse or be replaced easily and continuously by fresh acid so that a high rate of dissolution may be maintained. These processes depend largely on accessibility i.e. on the size of the constriction to the cracks and channels, and an ease of passage through them. Sintering at high temperatures can cause partial or complete sealing of these cracks by diffusion of chromite or by the fusion of the gangue, making the leaching of metal more difficult or impossible. This theory is supported by the observed decrease in metal extraction with increased temperature of sintering, as shown in Table 20.

7.5 Effect of Carbon on the Amount of Acid-Soluble Iron and Chromium.

The proportion of carbon added to the concentrate was shown by earlier results (Table 20) to have a direct effect on the amounts of removal iron and chromium in the leaching stage. More information was therefore sought on the relationship between carbon addition and optimum iron extraction with minimum chromium loss.

Half inch briquettes were again used as in the previous series of tests (ref. Section 7.3). The amount of graphite added ranged from 0 to 8% and a 5% sodium chloride solution was used as binding agent. The briquettes were dried and fired to 1340^{o}C in the horizontal platinum tube furnace in an atmosphere of nitrogen as described in section 6.4. After soaking the briquettes at the maximum temperature for 5 mins. they were cooled to room temperatures

in a neutral atmosphere. They were then weighed and leached with 10% boiling sulphuric acid for 3 hours, when no further iron or chromium dissolved. The leached briquettes were removed and washed, and the leach liquor was analysed for iron and chromium. The results are shown in Figs. 29 and 30.

It can be seen that the amount of acid-soluble iron was approximately proportional to the amount of graphite incorporated in the briquettes up to 4% by weight (see Fig. 29). Beyond this value, the amount of acid-soluble iron tended towards a maximum but the amount of acid-soluble chromium increased rapidly. Although the chromium:iron ratio in the leached residue continued to increase, the percentage of Cr_2O_3 in the beneficiated product reached a maximum value with about 4% graphite and then decreased again (see Fig. 30).

Leaching the fired products in boiling 10% sulphuric acid is an extreme form of treatment. Another similar series of tests was, therefore, performed. The firing was conducted in the vertical molybdenum tube furnace to 1450^{o}C as described in Section 7.3. The fired products were discharged from the furnace at a temperature of about 200^{o}C directly into 10% sulphuric acid at room temperature. Leaching was continued for 100 hours until no more metal appeared to dissolve. The results of the leaching tests are shown in Figs. 31 and 32, indicating a trend very similar to that of the preceding series with boiling 10% sulphuric acid.

FIG 29

EFFECT OF GRAPHITE ON ACID SOLUBLE IRON & CHROMIUM

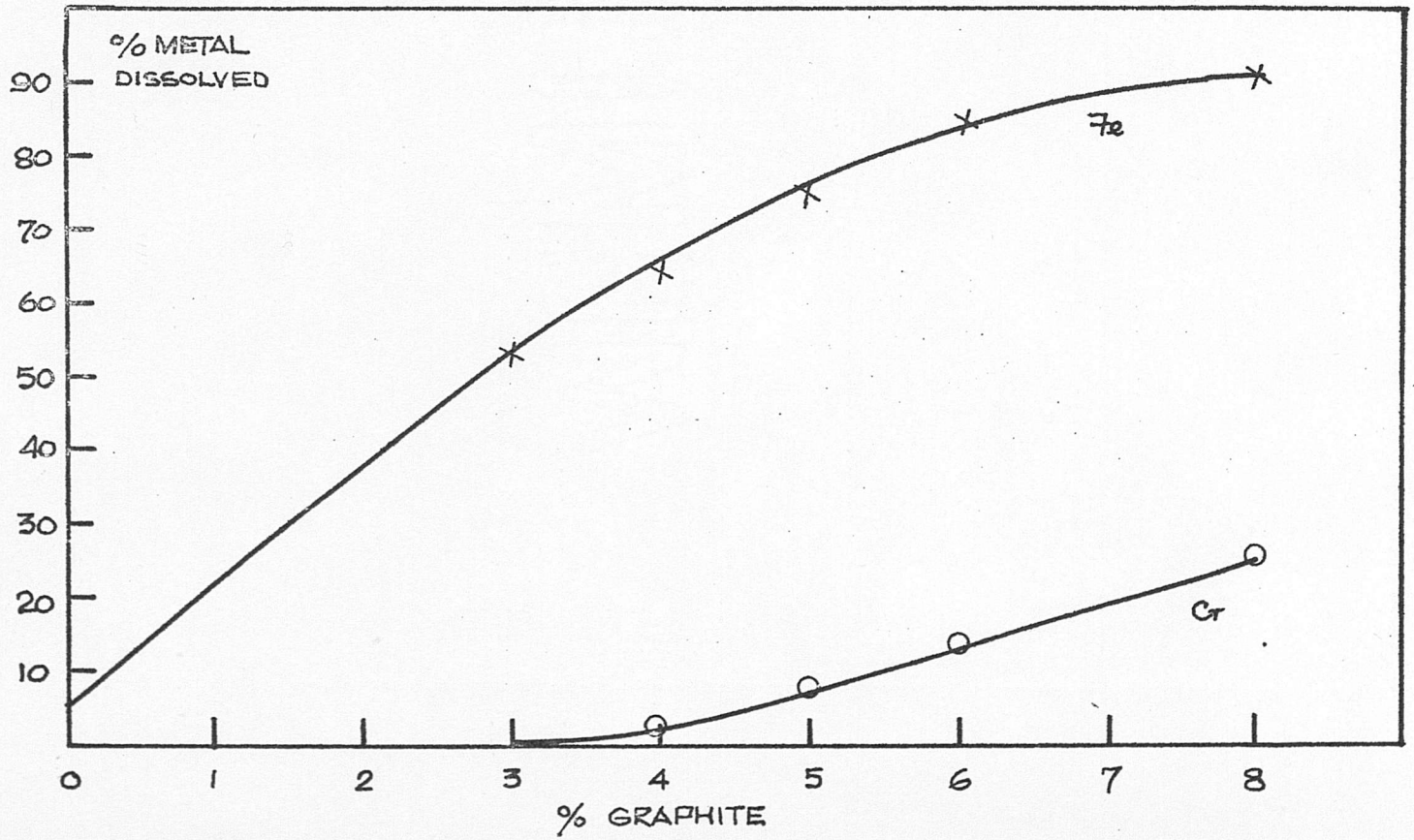


FIG 30

EFFECT OF GRAPHITE ON GRADE OF PRODUCT

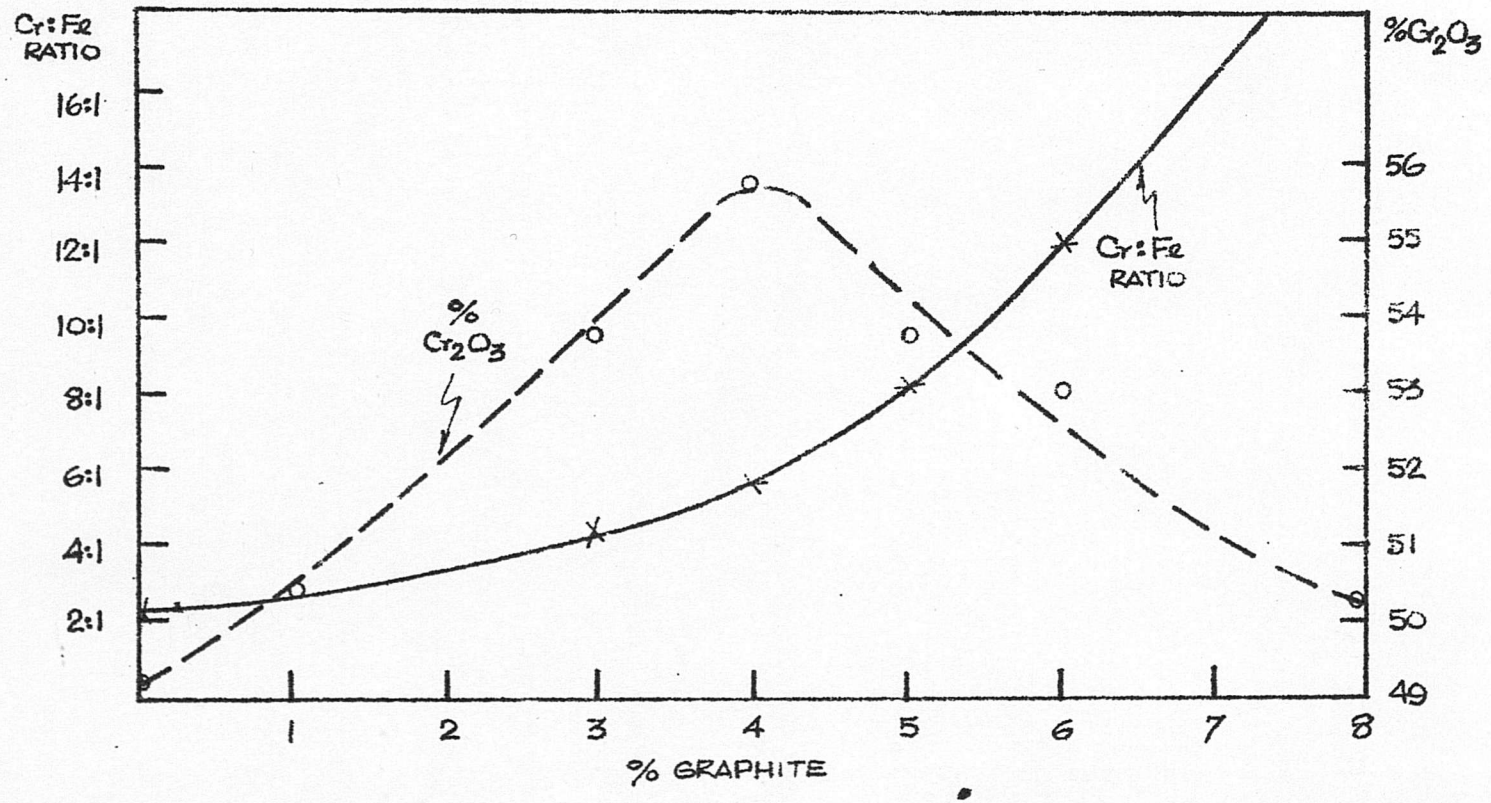


FIG 31

EFFECT OF GRAPHITE ON ACID SOLUBLE IRON & CHROMIUM

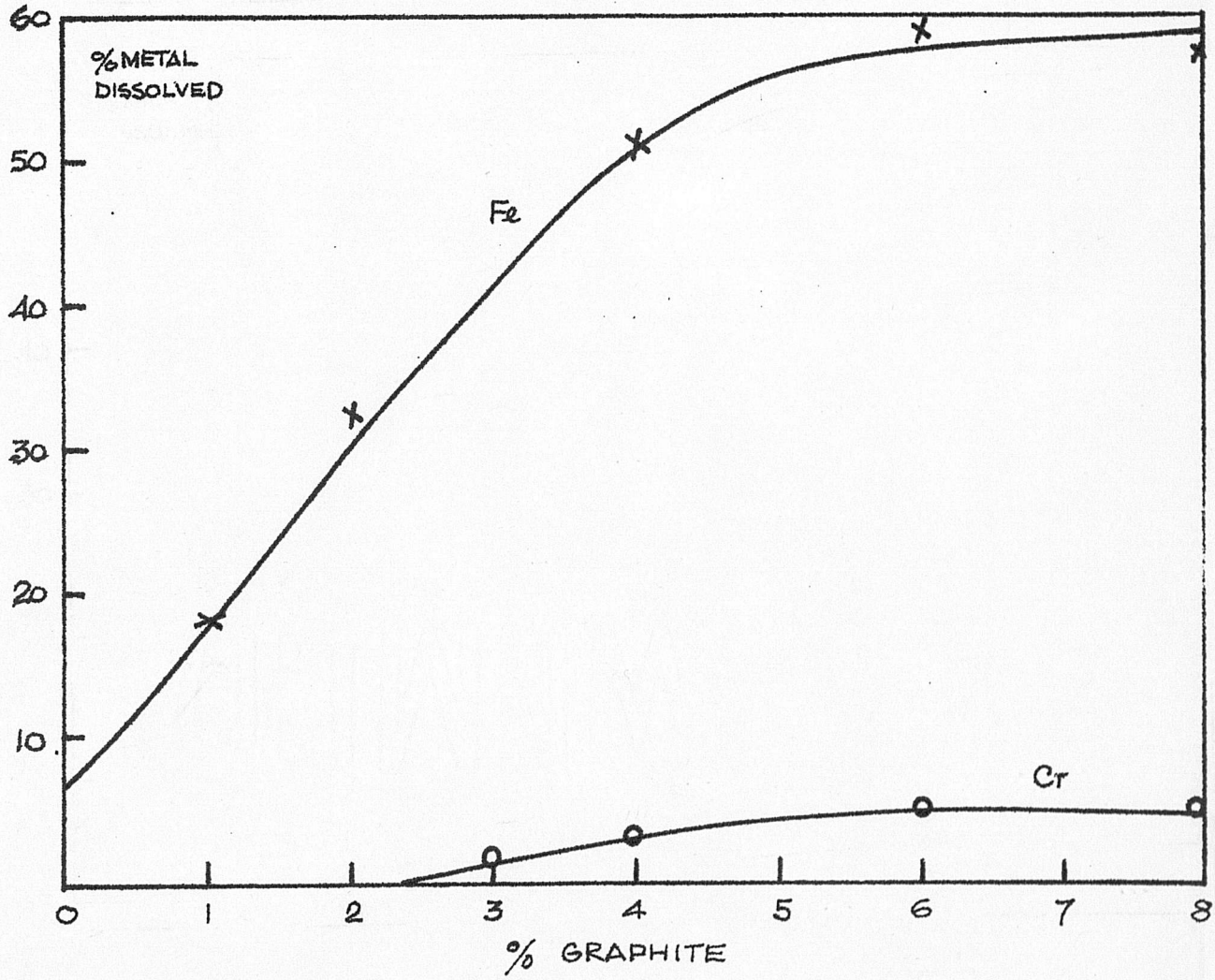
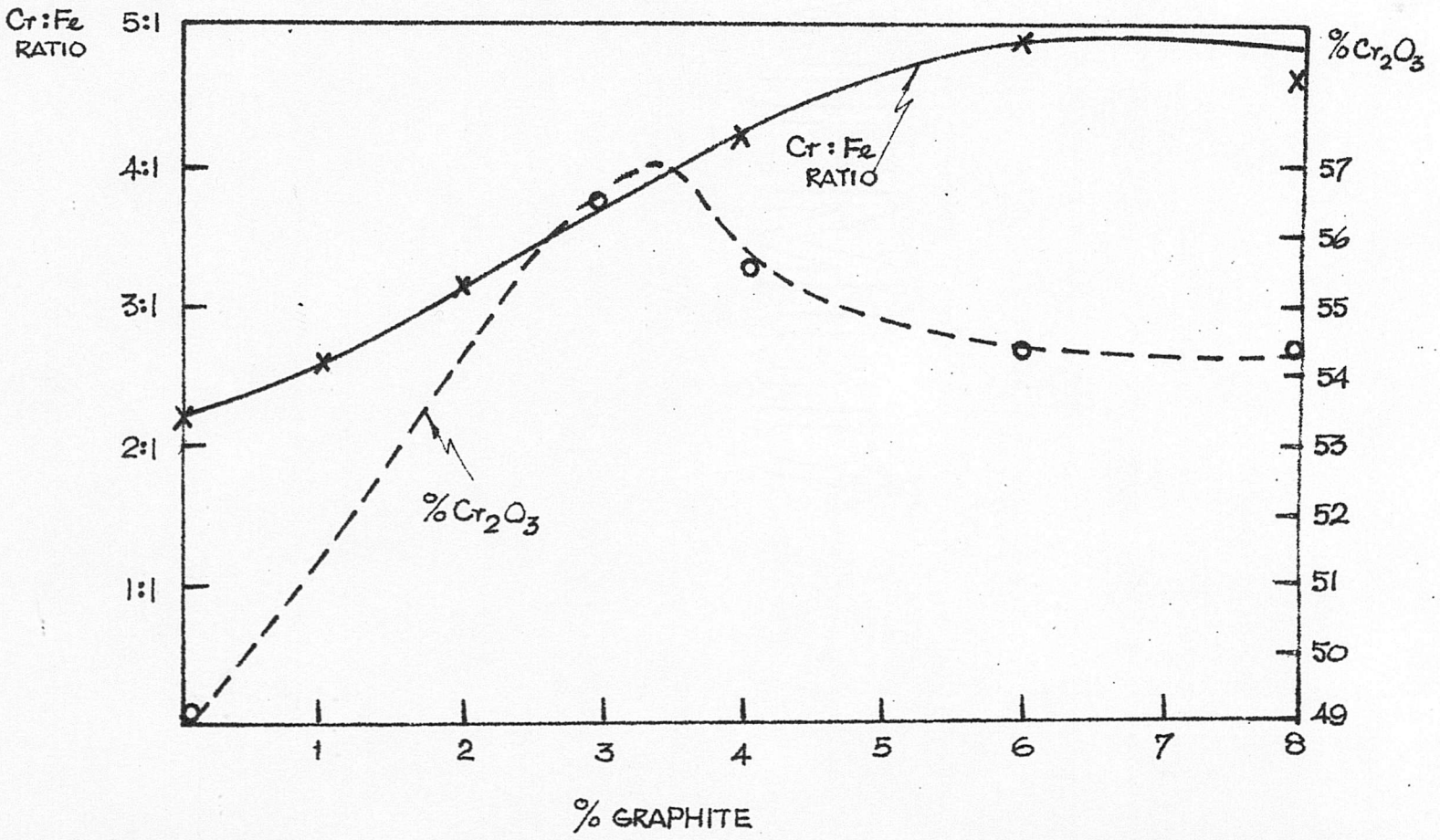


FIG 32

EFFECT OF GRAPHITE ON GRADE OF PRODUCT



The theoretical amounts of graphite required to reduce all the iron oxide in chromite to metallic iron is of the order of 3.4%. The above results show that the actual consumption of graphite in the process was considerably higher. Metal extraction in all the tests accounted for only 40-50% of the graphite used. This was at least partly due to the incomplete extraction of the reduced metals from the briquettes during leaching. However, examination of polished sections (see Section 7.12) showed that, although some metals remained in the leached residue, the amount was less than 40-50% of the total metal produced. The unaccounted carbon could probably be consumed in the formation of carbides.

7.6 The Effect of Dwelling Time in Various Temperature Zones on the Removal of Iron and Chromium.

The inadequate extraction of iron during leaching was thought to be due partly to occlusion of metal by the sintering of gangue and chromite and partly to the formation of carbides at high temperatures. Attempts were, therefore, made to alter these defects by conducting sintering for different lengths of time at different temperatures in the hope of obtaining more efficient removal of iron.

As before, ½" briquettes were used with 4% graphite and a 5% sodium chloride binding solution. After firing, the briquettes were leached in boiling 10% sulphuric acid for 3 hours. The results of the test are shown in Table 21.

It was found that reduction at 1150°C was slow, a dwelling time of 15 min. being inadequate for complete reaction with all the graphite available. Free graphite was still detectable in the acid during leaching. A dwelling time of 80 min. was needed for eliminating all the free graphite. The speed of reaction was more rapid at higher temperatures. At temperatures above 1300°C, a dwelling time of 3 to 5 min. was sufficient for all the carbon to react with the mineral.

The results, shown in Table 21, indicate that the residence time in the furnace is relatively unimportant with respect to metal extraction, provided all the graphite had been reacted. Runs 1, 2 and 3 in Table 21 show only small differences in the extraction of iron. The maximum temperature of treatment affects the process to a much greater extent (also see Table 20) and reduction at a lower temperature produced more extractable metal than reduction at a high temperature (compare runs 3 and 5 in Table 21).

By contrast, the strength of the briquettes is markedly affected by the dwelling period in the furnace. Stronger briquettes being produced with longer periods of residence (compare runs 2 and 3, Table 21). This effect is enhanced when the extra period of sintering occurs at the maximum temperature (compare runs 1 and 2 in Table 21)

TABLE 21.

Effect of Dwelling Time in Various Temperature Zones on the Amount of Removable Iron and Chromium

Run No.	Mode of Firing	Max. Temp. of Firing (°C)	Dwelling time in Temp. Zone (min)		Metal Extracted (%)		Grade of Product		Radial Compressive Strength (Kg)
			1150°C	1390°C	Cr	Fe	Cr : Fe	% Cr_2O_3	
1	Mo. Furnace	1390	$2\frac{1}{2}$	25	3.5	72.1	7.3	56.2	145
2	" "	1390	25	$2\frac{1}{2}$	3.7	72.8	7.3	54.8	125
3	" "	1390	$2\frac{1}{2}$	$2\frac{1}{2}$	3.8	75.3	8.2	55.8	75
4*	Pt. Furnace	1150	15	-	2.1	54.4	4.5	55.4	20
5	" "	1150	80	-	4.1	84.2	12.7	55.8	35

* Reduction incomplete, free graphite detected in leach liquor

% Graphite for reduction 4%

Binding agent 5% Na Cl solution

Acid for leaching Boiling 10% H_2SO_4

It is concluded that the increased strength of the fired briquettes is caused by better sintering of the chromite. The extra dwelling time provides a longer period of solid diffusion, recrystallization and more extensive formation of a glassy matrix, resulting in better bridging between the grains and more extensive sealing of cracks and channels inside the chromite particles. Any iron deposited in such places, thus becomes less accessible to the acid during leaching. Consequently weaker briquettes produced at a low temperature of firing, yield a larger amount of acid-soluble iron than briquettes fired to a much higher temperature.

No changes in the mode of deposition of acid-soluble iron resulted from altering the rate of reduction and no migration of metallic iron from the cracks to the surface of the grains took place at low temperatures even with prolonged dwelling periods (see Plates 10 and 11).

7.7 The Effect of Concentration of Sodium Chloride Solution on the Reduction and Leaching of Iron and Chromium

The use of sodium chloride solution as a binder resulted in a larger amount of acid-soluble iron than any of the additives tried in this work. Its effect on the reduction and leaching processes hence merited further investigation.

Briquettes were made with different concentrations of sodium chloride solution together with 2% graphite. They were

fired in the horizontal platinum tube furnace to 1340°C for 5 min. The fired products were subjected to axial compression test and then leached in 10% H_2SO_4 under boiling conditions for 3 hours. The results are shown in Table 22.

TABLE 22

Effect of Concentration of NaCl Binding Solution on the Compressive Strength of Briquettes and the Extraction of Iron and Chromium

Concentration of NaCl Solution	% of Metal Extracted		Radial Compressive Strength in kg. (size of briquette $\frac{1}{2}$" diam. x $\frac{1}{3}$" thick)
	Cr	Fe	
0%	0.3	35.1	80
5%	0.3	34.8	105
10%	0.3	33.2	135
20%	0.3	32.0	165

% Graphite for reduction - 2%

Max. temp. of sintering - 1340°C in pt. tube furnace.

Acid for leaching - Boiling 10% H_2SO_4

It can be seen that the fired strength of the briquettes increased with an increasing concentration of sodium chloride binding solution, but the amount of extractable iron in the briquettes assumed an opposite trend. It was concluded that a strength of sodium chloride solution of up to 5% may be employed without adverse effects on the amounts of extractable metals.

It was further concluded that the presence of high amounts of sodium chloride can create better sintering but does

not encourage migration of iron from the interior to the surface of the chromite particles and no increase in the size of the particles of iron was observed.

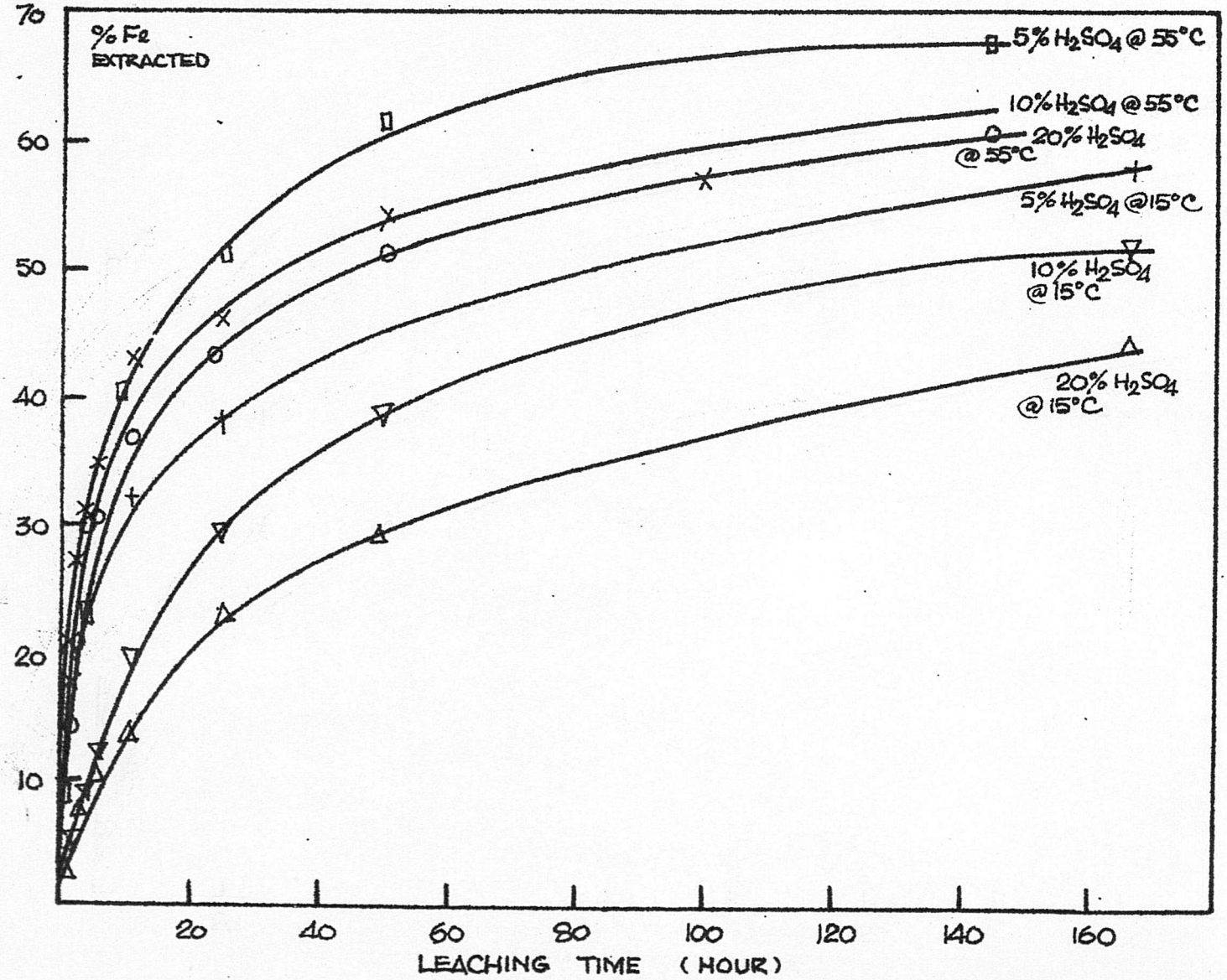
7.8 Rates of Leaching of Iron and Chromium.

In this investigation indentical briquettes (see Section 7.9) were leached in acid of various concentrations at different temperatures and samples of the leach liquor were taken at regular intervals for iron and chromium determinations. The curves for the leaching rates of the two metals were obtained and are shown in Figs. 33 and 34.

The leaching rates for iron was found to be different from that for chromium. At the onset of the leaching operation, a large amount of iron was taken into solution rapidly. The rate of dissolution then decreased until no further significant amount of iron could be extracted. In contrast, comparatively little chromium was dissolved at the beginning of the leach but the amount of chromium dissolved did not decrease much even after a long leaching period. This was indicated by Fig. 35 which shows leach liquors with very high iron:chromium ratio at the beginning of the leach but lower iron:chromium ratio after 20 minutes. A possible explanation for this phenomenon is that the acid-soluble iron may form a coating on the acid-soluble chromium. When leaching commences, the iron is dissolved first and chromium is little affected until the coating of iron has been removed.

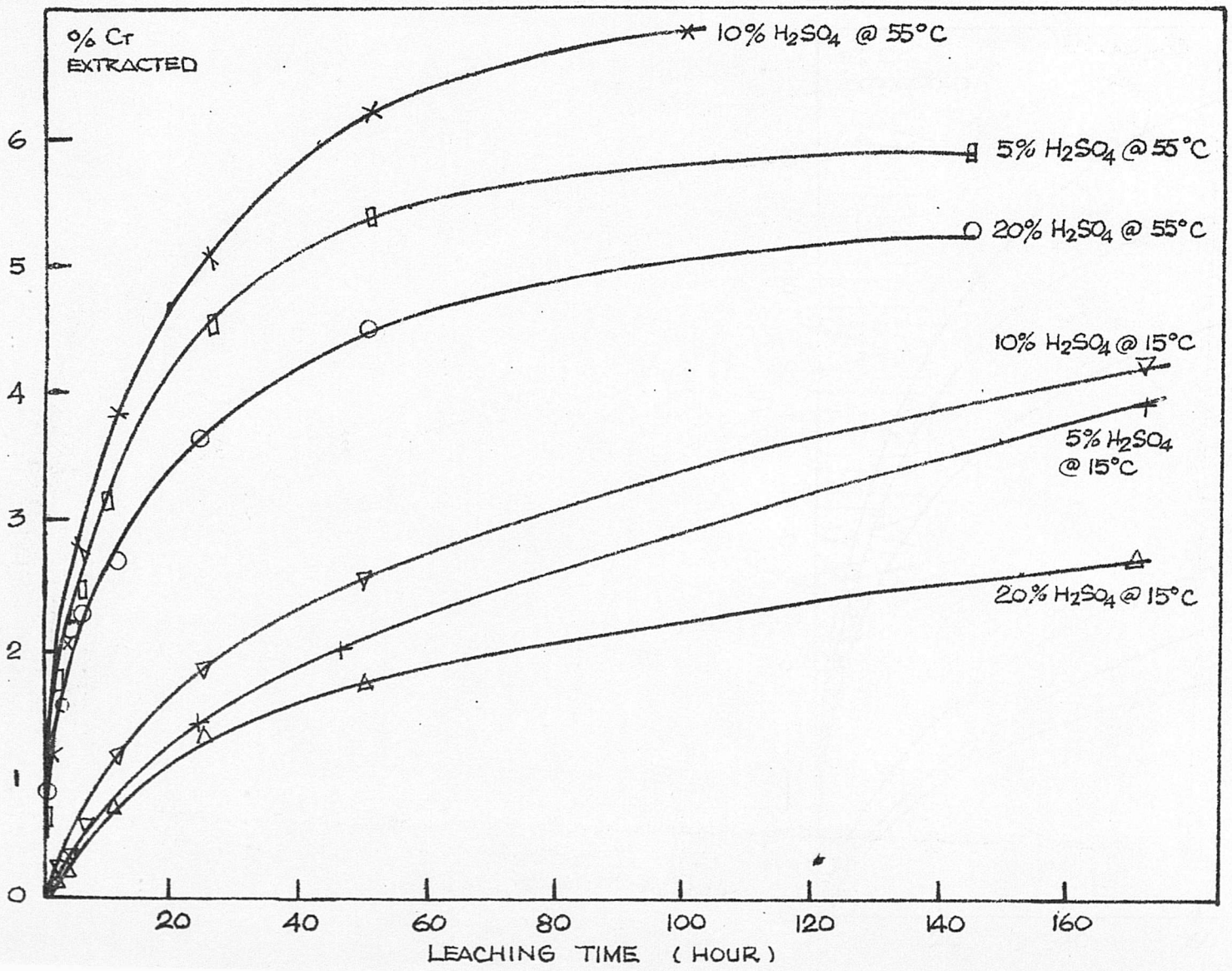
LEACHING OF IRON FROM REDUCED CHROMITE

FIG 33



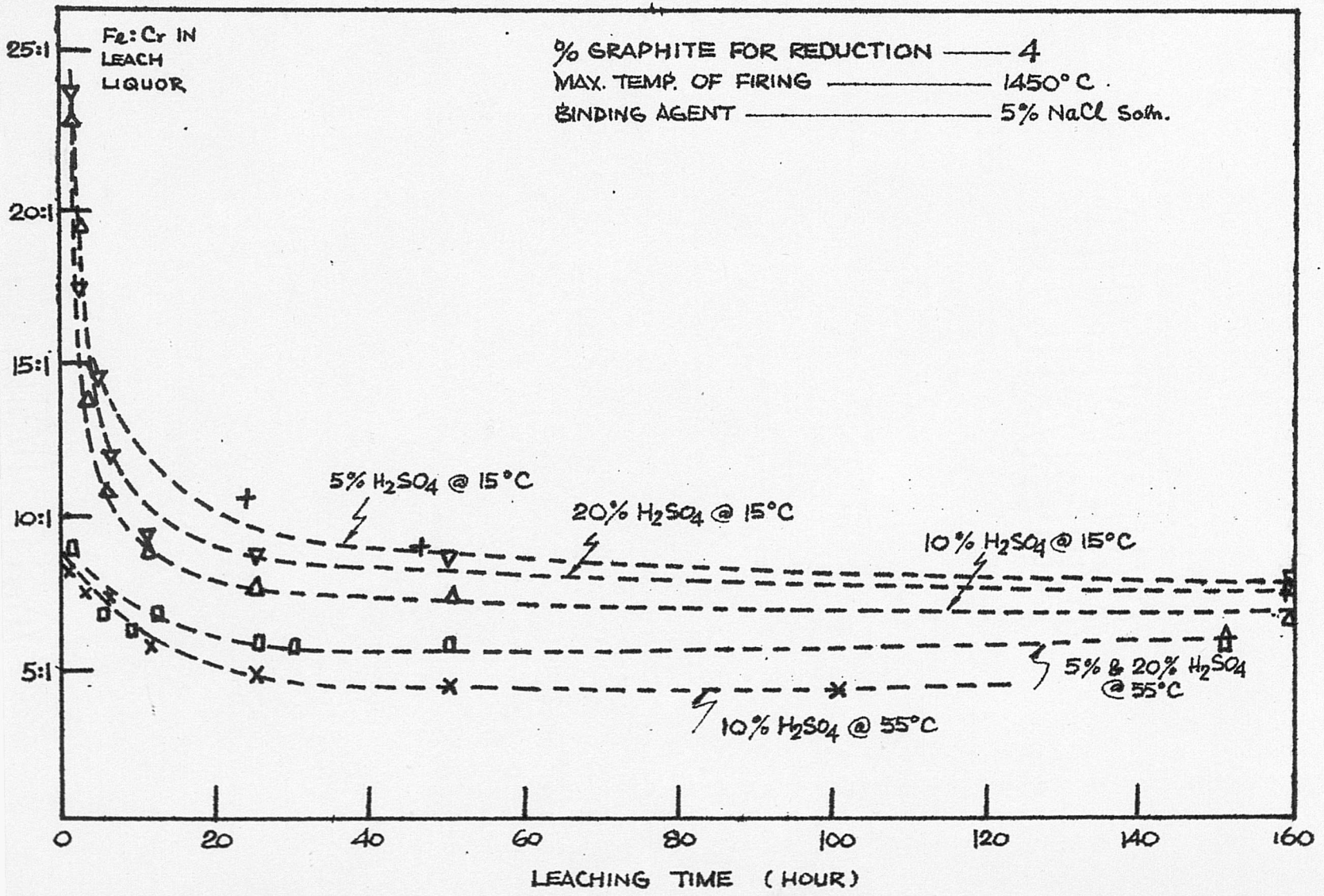
LEACHING OF CHROMIUM FROM REDUCED CHROMITE

FIG 34



RATIO OF IRON : CHROMIUM REMOVED DURING LEACHING

FIG 35



The overall rate of dissolution at 55°C is much higher than at room temperatures (see Figs. 33 and 34). At boiling point, complete extraction occurs within three hours. The increased rate of dissolution at elevated temperatures is presumed to be due to higher rates of diffusion in the liquid.

7.9 Effects of Temperature and Concentration of Sulphuric Acid on the Leaching of Iron and Chromium.

The removal of iron and chromium from the reduced briquettes may be expected to be influenced by the concentration and temperature of the acid. Boericke and Bangert (13) observed that hot 10% sulphuric acid could remove more iron and chromium than cold acid of the same concentration and that this tendency became more evident when the chromite concentrate was over reduced. Careful control of the temperature of leaching in order to avoid excessive solution of chromium was also emphasised in an attempt to leach chromite at high temperatures and pressures (7).

To investigate the effects of temperature of leaching and acid concentration, identical briquettes were again prepared and fired under reducing conditions in the vertical molybdenum tube furnace at 1450°C with 4% graphite and 5% sodium chloride solution as binding agent. The fired products were cooled to room temperature (15°C) and were then leached in acid solutions of various concentrations and at different temperatures. The results are shown in Figs. 33, 34 and 35 and Table 25.

TABLE 25.

Effect of Temperature of Acid on Extraction of Iron and Chromium

Temperature of Acid		100°C		50°C		15°C	
		Cr	Fe	Cr	Fe	Cr	Fe
% of Metal Extracted	A	5.7	65.8	5.6	63.3	3.9	57.8
	B	6.8	57.3	6.8	56.9	4.2	52.2
Cr:Fe ratio in product	A	5.8		5.5		4.8	
	B	4.6		4.6		4.2	
% Cr_2O_3 in product	A	54.0		54.2		55.0	
	B	53.5		53.5		54.8	

% Graphite for reduction - 4%

Max. temperature of firing - 1450°C

Mode of firing - Continuous process in vertical molybdenum tube furnace

Binding agent - 5% NaCl solution

Acid used for leaching - A, 5% H_2SO_4
B, 10% H_2SO_4

The results indicate that the extraction of iron was more efficient at 55°C than at room temperature but little change in the extraction of iron was observed between leaching at 55°C and leaching at boiling point of the acid solution (see Table 25). The higher extraction of iron at an elevated temperature was accompanied by a proportionally higher chromium loss and leaching at high temperatures, hence, appears to be less selective. Boericke and Bangert (13) attributed this to

the different solubilities of various carbides of iron and chromium.

The concentration of the acid was also found to affect the removal of acid-soluble metals. A 5% sulphuric acid leached a maximum of 63.3% iron at 55°C and a 10% acid leached 56.9% iron at the same temperature. Chromium, on the other hand, was less readily attacked by 5% sulphuric acid than by 10% acid. The former dissolved a maximum of 5.6% at 55°C and the latter 6.8%, all other conditions being equal.

The decreased removal of iron by more concentrated acids may be due to the passivation of iron in the briquettes. Concentrated sulphuric acid is a strong oxidizing agent and, therefore it is possible that a layer of oxide (Fe_2O_3) insoluble in acid is formed on the metal surface, preventing further acid attack (66).

The maximum selectivity in the removal of iron from the reduced material was obtained with acid of low concentration at room temperatures. A 5% acid extracted 57.8% iron and 3.9% chromium, resulting in having a product containing 55.0% Cr_2O_3 with a chromium:iron ratio of 4.8:1, after over 100 hours of leaching. The very slow rate of dissolution, however, renders this procedure impracticable. The best compromise appears to be leaching the agglomerates at a higher initial temperature (near boiling) for a short period up to about 5 minuts (see Fig. 35), followed by more prolonged leaching at lower temperatures (room temperatures). During the initial stage, the rate of dissolution

of chromium would be slow and a rapid removal of iron would be possible without adverse effects on chromium recovery. The subsequent lowered temperature of leaching would yield more iron but would keep the dissolution of chromium at a low rate. Quenching of the hot product from the furnace by discharging the agglomerates directly into the acid at room temperatures appears to be a simple method of attaining this combination of conditions without recourse to external heating of the acid solution.

7.10 Effect of Quenching Hot Briquettes in Acid on the Removal of Iron and Chromium.

An investigation of quenching hot briquettes directly in the acid was carried out with ½" briquettes fired for 5 min. at 1340°C. in the horizontal platinum tube furnace. They contained 4% wood charcoal as reducing agent and 5% sodium chloride solution as binder. After firing, the partially cooled briquettes were quenched in 10% sulphuric acid at room temperature. The briquettes cooled rapidly in the acid where they were leached until no more iron or chromium dissolved. The results are shown in Table 23.

Little difference was observed in the maximum extraction of iron and chromium on comparing quenching the briquettes from 250°C and no quenching. However, the overall rate of dissolution was much higher when the briquettes were quenched. Over 100 hours were required to obtain maximum leaching from cold briquettes when no quenching was applied. By contrast, complete extraction could

TABLE 23

Effect of Quenching Temperature on Extraction of Iron and Chromium

Temperature of Quenching	% of Metal Extracted		Grade of Product	
	Cr	Fe	Cr : Fe	% Cr_2O_3
400°C	1.3	63.4	5.7	56.8
250°C	1.3	55.8	4.7	56.0
15°C (room temp.)	1.3	55.3	4.7	55.8

% Wood charcoal for reduction - 4%

Max. temp. of firing - 1340°C

Mode of firing - Horizontal Pt. tube furnace

Binding agent - 5% NaCl solution

Acid used for leaching - 10% H_2SO_4 at 15°C

be achieved in under 30 hours without agitation when the briquettes were quenched from high temperatures, without decrease in the chromium recovery.

Quenching from 400°C in cold sulphuric acid resulted in a rise in the amount of leached iron from 55.3% to 63.4% as compared with leaching without quenching. The removal of a higher amount of iron by quenching from 400°C is probably due to the more complete extraction of iron deposited in the cracks, occluded by fused gangue materials. Sudden quenching from high temperatures resulted in the shattering of the glassy matrix of

gangue, permitting penetration of acid to reach the trapped iron. Owing to the small amount of gangue present the shattering of fused gangue was difficult to observe under the microscope. However, it has been reported (67) that rapid cooling of iron ore sinters could result in the development of cracks running through the slag bond. It is, therefore, concluded that similar mechanism may be responsible for more efficient leaching of the agglomerates.

7.11 Effect of Using Other Organic Materials as a Binding/Reducing Agent

Although graphite and wood charcoal have been successfully applied as reducing agents in this investigation; the use of other organic materials as combined binding/reducing agent was considered an attractive alternative. Treacle and heavy lubricating oils were chosen as representatives of this kind of additives.

Half inch briquettes were again used and firing was conducted in the horizontal platinum tube furnace at 1340^{o}C. Leaching was performed in boiling 10% sulphuric acid for 3 hours. The results are shown in Table 24.

Owing to the low surface tension of the oils investigated, the green briquettes formed with oil binders were found to be very brittle and tended to disintegrate on firing. On heating, the oils were distilled off at temperatures too low for reduction and sintering to occur. Only a very small amount of acid-soluble iron was, therefore, produced and the compressive strength of the fired

TABLE 24

Effect of Using Other Organic Material as a Binding/Reducing Agent

Binding/Reducing Agent	% of Metal Extracted		Grade of Product		Radial Compressive Strength of Fired Briquettes
	Cr	Fe	Cr : Fe	% Cr_2O_3	
4% Graphite + 5% NaCl solution	2.9	69.0	6.7	55.8	100 kg
4% Wood Charcoal + 5% NaCl soln.	1.8	64.6	5.8	56.0	85 kg
Brown Treacle	0.9	17.7	2.6	52.2	105 kg
SAE 50 Willcox Lubricating Oil	0.6	10.8	2.4	49.4	Disintegrated
Shell Mex Dromus Oil B	Negligible	8.9	2.3	49.2	75 kg

Max. temp. of firing - 1340°C (Horizontal Pt. tube furnace)

Acid used for leaching - Boiling 10% H_2SO_4

briquettes was low (see Table 24). Brown treacle on the other hand, produced exceptionally strong green and dry briquettes. Its efficiency as a reducing agent was, however, not comparable to those of graphite or wood charcoal. The treacle decomposed and the amount of carbon remaining in the briquettes for reduction was probably small. Although this line was not pursued any further, it is suggested that a process employing treacle as binder and wood charcoal as reducing agent could give strong unfired and fired pellets with a high chromium:iron ratio.

7.12 Study of Polished Sections and X-Ray Microradiographs.

Assessment of the mechanisms and effects of the processes under investigation was not confined to physical and chemical tests, but was further supplemented by visual examination of samples before and after treatment, using techniques of reflected light microscopy (61) and microradiography (95). In this connection, polished sections and thin sections of various specimens were prepared and some photographs of the observations are shown in Plates 5, 6, 7, 8, 9, 10 and 11.

Plate 5 shows the polished section of untreated chromite grains. The grains are generally granular in shape with occasional protruding edges. All of them possess cracks and channels leading from the exterior to the centre of the grain. No metallic iron or any sign of heterogeneity was visible in the polished section.

On firing the agglomerates of fine chromite concentrate to a high temperature the points of contact of the particles fuse together forming bridges, binding adjacent particles, as shown in Plate 6. Similar mechanism of sintering of gangue particles was also observed (not shown in photograph) and in addition sintering between gangue and chromite particles also occurred extensively. In the absence of a reducing agent no metallic iron or chromium was visible. Although the outlines of the various particles tend to be smoother, no complete recrystallisation of chromite grains was observed at 1420°C (ref. Section 6.5).

At firing temperatures in the region of 1500°C in the presence of a reducing agent, a highly reflective malleable metal, resembling metallic iron, segregates from the original chromite grains as shown in Plate 7. Some of this iron was deposited in the interstitial spaces in the briquettes as stringers, globules, and lumps of irregular shapes and sizes while some iron was deposited in the narrow cracks and channels inside the chromite particles. The iron when deposited outside the grain was sometimes completely or partially occluded by fused gangue materials. As for the iron deposited inside the chromite grain slag sealing at the entrance to the cracks and channels was often observed. The location of iron is further confirmed by the study of micro-radiograph as shown in Plates 3A and B, Section 6.5. It can, therefore, be concluded that the production of metallic iron is

due to reduction by carbon at high temperatures.

Plate 8 shows the polished section of a chromite briquette which had been reduced by 4% graphite at 1340°C and leached in sulphuric acid. It can be seen that the metallic iron was removed completely, except for some which were deposited in the cracks and channels. These channels were observed to be sealed by gangue material or to be too constricted for efficient acid penetration during leaching. This was a probable cause for the incomplete extraction of iron.

The amount of residual iron is greater in briquettes fired to 1500°C than those fired to 1340°C. Plate 9 indicates that most of the openings to the cracks and channels were more constricted, and sealing by gangue material was more extensive with an increase in sintering temperature, confirming earlier suggestions.

In view of the unfavourable location of metallic iron in the cracks and channels of the grains, work was directed towards the attainability of a more favourable reducing condition in which better acid accessibility could be achieved. Briquettes were, therefore, prepared and fired as described in section 7.6 and the photographs of polished sections of specimens are shown in Plates 10 and 11.

Plates 10 and 11 show that some of the iron was still located in the cracks in the chromite grains and there was no

indication that migration of iron from the interior to the surfaces of the chromite particle had occurred. The differences in the amounts of extractable iron from the briquettes as described in Section 7.6 can, therefore, be attributed to different degrees of sintering resulting in different extents of iron occlusion.

During the examination of various polished sections of chromite briquettes, it was observed that the amounts and location of the metallic iron in the briquette were independent of the nature of the binding agents employed. The amount of iron present before leaching depended mainly on the quantity of carbon incorporated for reduction; a higher degree of reduction produced a larger amount of metallic iron.

Metallic chromium has an almost similar reflectivity as iron. In view of the small amount of acid-soluble chromium present, its location in the reduced material has not been established.

7.13 Study of X-Ray Diffraction-Powder Photographs.

X-ray diffraction powder photographs of material before and after treatment were obtained using cobalt K_α radiation. It was thought that changes in the structure of the chromite spinel might be revealed by changes in the diffraction patterns in the powder photographs.

The lines produced by the head sample and the reduced

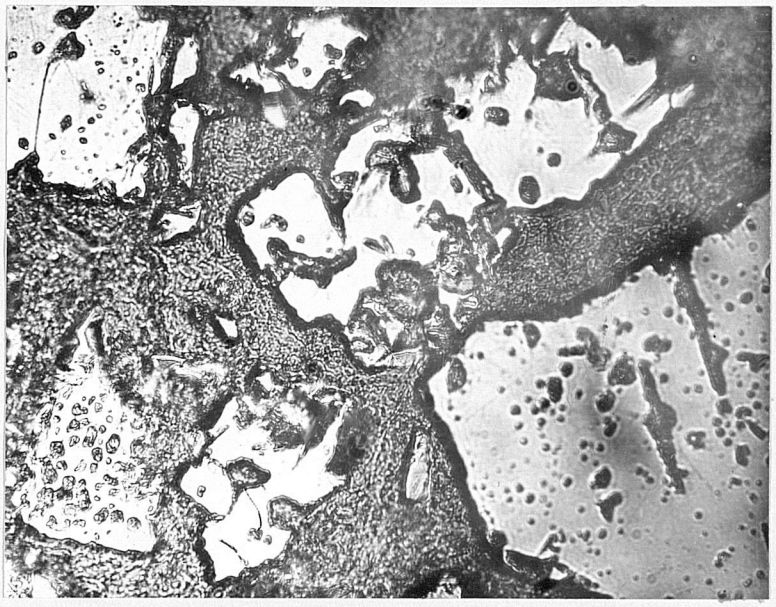


PLATE 5.

Polished Section of Untreated Chromite.

(x570)

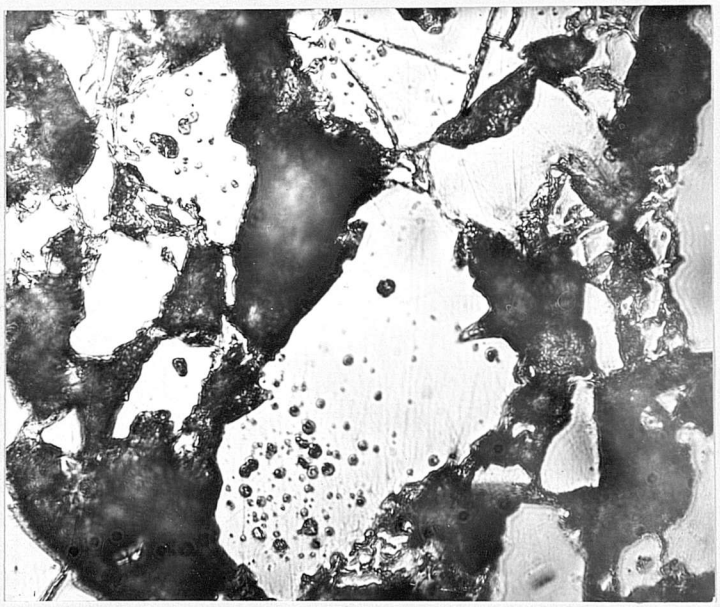


PLATE 6. Polished Section of Chromite Briquette Sintered at 1420°C in Neutral Atmosphere.

(×570)

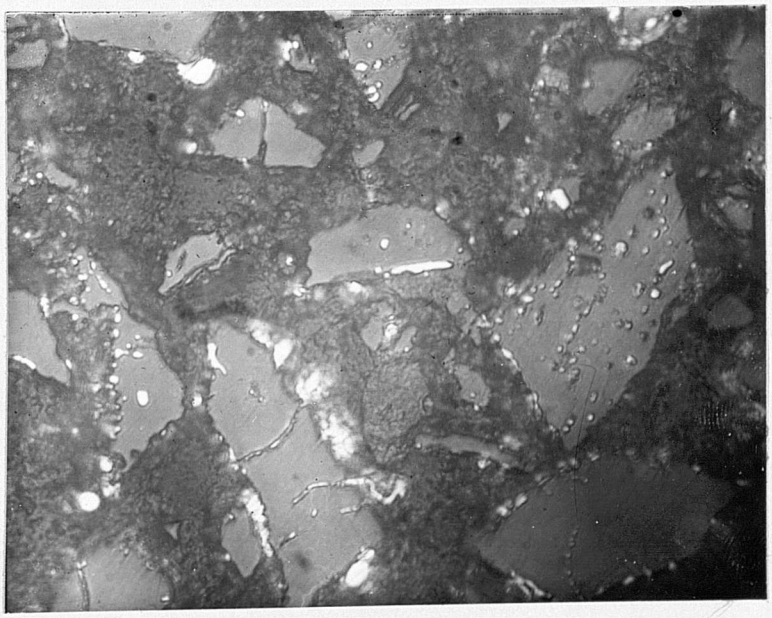


PLATE 7. Polished Section of Chromite Briquette Sintered at 1500°C in Reducing Atmosphere.

(×570)



PLATE 5. Polished Section of Reduced and Leached Chromite (Temp. of Sintering 1340°C).

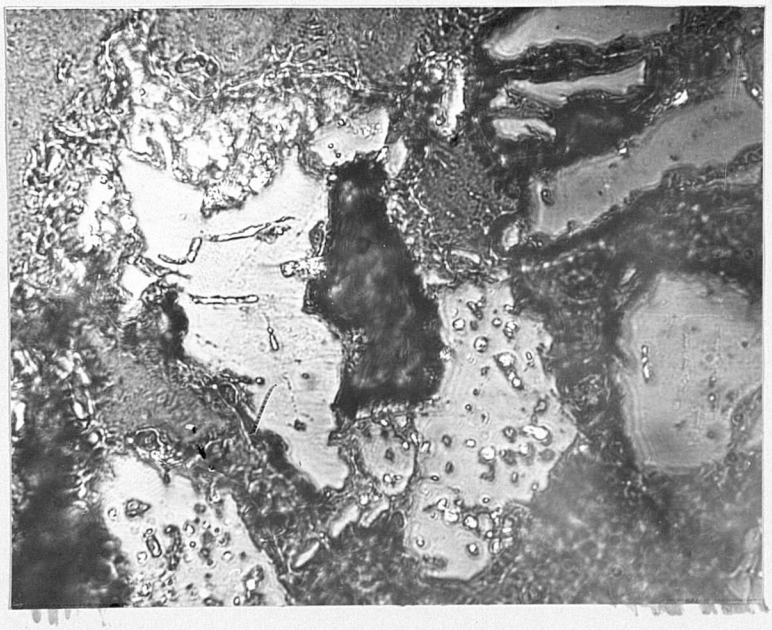


PLATE 6. Polished Section of Reduced and Leached Chromite (Temp. of Sintering 1500°C).

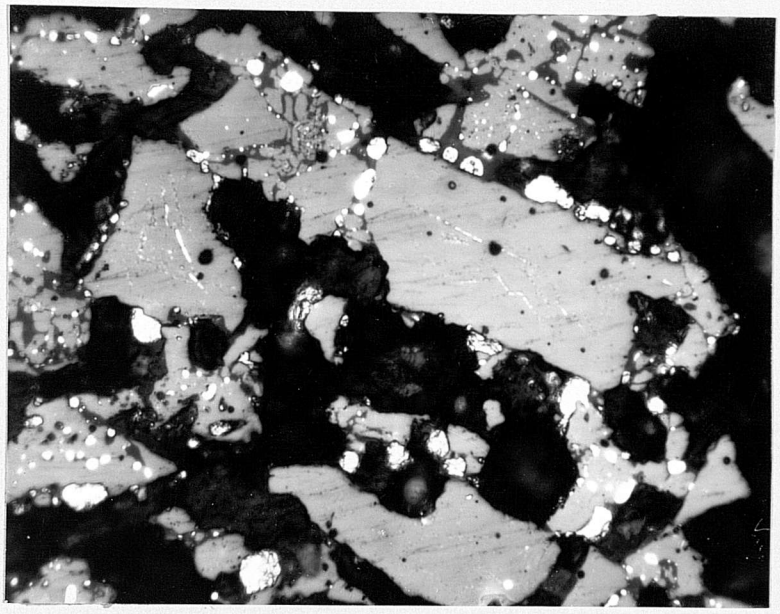


PLATE 10. Polished Section of Chromite Fired Rapidly to 1500°C with 4%C.

(x570)

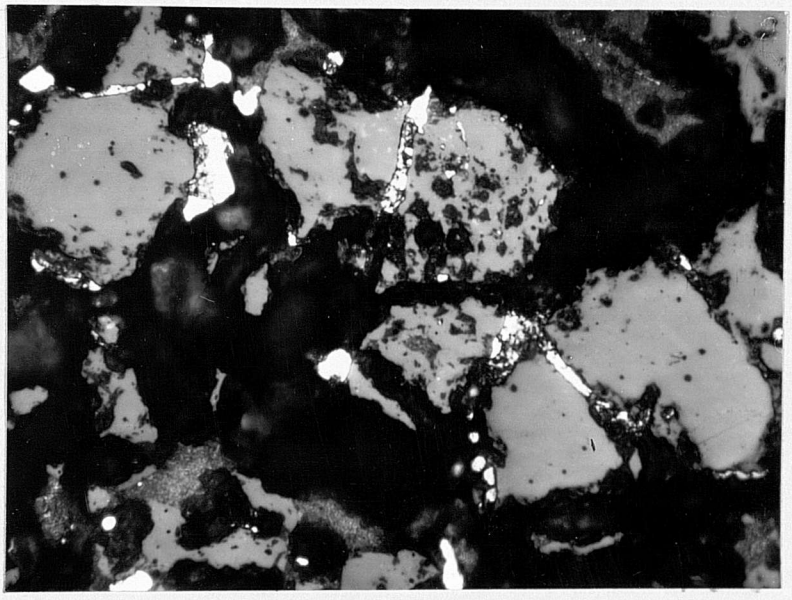


PLATE 11. Polished Section of Chromite Fired to 1390°C After Soaking for 15 Min. with 4%C.

(x570)

and leached products were identical. The three prominent lines correspond to 2.5Å, 1.59Å and 1.46Å. These correspond to those of chrompicotite $(Fe, Mg)O.(Cr, Al)_2O_3$ or chromite $(FeO)(Cr, Al)_2O_3$ as reported in the A.S.T.M. index. These lines were not affected by the degree of reduction or the amount or nature of binding agents present in the briquettes. The reduced material which was not leached, however, also showed the lines of metallic iron. However, it should be noted that crystalline phases present in proportions smaller than 5% (by weight) cannot be detected by this method of analysis.

It is concluded that the removal of iron and oxygen from the chromite spinel during reduction does not alter the basic crystal structure of the remaining material.

8.0 SUMMARY OF CONCLUSIONS

A chromite concentrate from Southern Rhodesia, containing 43.8% Cr_2O_3 with a chromium:iron ratio of 2.1:1, was treated successfully by a sequence of processes of pelletizing; high temperature hardening and reduction; and leaching with sulphuric acid. This yields a lumpy, porous end product, containing over 55% Cr_2O_3, with a chromium:iron ratio in excess of 4:1 and a chromium recovery of 98% or higher. Graphite or wood charcoal was used as reducing agents.

The salient features of the process and the main conclusions drawn from this may be summarised as follows:

Pelletizing:

1) Fine chromite concentrate containing 90% -150 mesh and 15% -200 mesh can be agglomerated into ½" pellets using either a dry or a wet feed in a laboratory drum.

2) For the attainment of a steady process and a consistent quality of the product, "seeding" of the load and employment of a wet feed are essential.

3) Although a feed containing up to 12.5% moisture can be employed, the optimum moisture content of the feed is 10.0-10.5% and that of the seeds, 9-10%. Further addition of water by spraying is not required under these conditions.

4) For a given drum, the rate of adding fresh feed has a marked influence on the circulating load of the process. A low feed rate produces a high circulating load, whereas a high feed rate results in a low circulating load.

5) The effect of the feed rate on circulating load is less apparent in a large drum than in a small one.

6) The peripheral velocity of the drum affects the mixing of the seeds and the feed and hence the rate of pellet growth. The optimum peripheral velocity under laboratory pelletizing conditions is 125 ft./min.

7) The compressive strength of the newly formed pellets is low, but is raised by further rolling.

8) Progressive compaction and stronger physical interlocking of particles in the pellets can be obtained during the initial stages of rolling.

9) Centrifugal action and compaction result in the migration of water from the core to the shell of the pellets where evaporation takes place rapidly. This causes a general reduction in moisture content.

10) The compressive strength of green pellets is due mainly to:

a) Physical interlocking of the particles and

b) Wet bonding by "pendular" liquid in the pellets.

11) The wet strength of the pellets increases as the moisture content decreases to 7.8% (by weight); with any further decrease in moisture content, the strength falls again.

12) A large rolling load in the drum is desirable for achieving high strength through good physical interlocking.

13) A small rolling load in the drum is advantageous if rapid removal of water is desired.

14) The drum should rotate at speeds which induce efficient pellet rolling but cascading of the load should be avoided.

15) Evaporation of liquid from a pellet results in the deposition of salts at is surface. This is attributed to capillary effects and to the surface tension gradient during drying.

16) Bonding of particles in a dried pellet is partly due to cementation by the salt deposit. This bonding is hence affected by the cleanliness of the surface, the mode of deposition of the salt and the nature of the salt.

Hardening:

1) Sintering at temperatures in excess of 800^{o}C is essential for the hardening of pellets.

2) Binders capable of preventing the disruption of chromite pellets during rapid heating are bentonite clay, sodium chloride, sulphuric acid, ferrous sulphate and sodium sulphate.

3) These binders also generally provide an increase in the dry and fired strengths of the pellets.

4) The effect of bentonite clay as a binder is reduced by the presence of sulphuric acid or sodium chloride.

5) Incorporation of graphite reduces the wet, dry and semi-fired (below 1200°C) strength of pellets.

6) Graphite promotes better sintering at temperatures above 1200°C, where reduction can proceed.

7) Sintering mechanisms at temperatures of 1200-1500°C comprises diffusion bonding between chromite and chromite, gangue and gangue, chromite and gangue. Iron bridges are also formed if conditions are sufficiently reducing.

8) At temperatures of over 1450°C diffusional bonding becomes more extensive. This is accompanied by almost complete fusion of gangue which then coats the surfaces of the chromite. Complete recrystallisation of chromite grains can also occur.

9) Pellets fired under oxidizing conditions are stronger than those fired under reducing conditions.

10) Pellets fired under an atmosphere of town gas disintegrated badly, and the shaft furnace with internal firing arrangements proved unsuitable for sintering.

Reduction:

1) Binding agents affect the amounts of leachable iron and chromium from reduced pellets

2) Sodium chloride was found to be the most suitable binder.

3) The optimum carbon content for reduction without excessive chromium losses is 4%. Organic materials such as treacle and heavy lubricating oil are unsuitable as reducing agents.

4) The metallic iron produced in the reduction process is deposited in the cracks of the chromite particles as well as in the voids of the pellets.

5) No preferential deposition of the metallic iron could be achieved by adjustments of firing periods and firing temperatures provided the temperature of reduction is above 1150^{o}C.

6) Reduction at a low temperature causes less extensive sintering and hence more efficient leaching of metallic iron. Reduction at high temperatures causes more extensive sintering and slag sealing of cracks, and, therefore, less efficient leaching of metallic iron.

7) Sintering at high temperatures has the advantage of providing higher pellet strength.

8) Extensive sintering and a consequent decrease in the amount of acid-soluble iron is also caused by the excessive incorporation of sodium chloride. A 5%

sodium chloride solution can be used as binder without adverse effects.

Leaching:

1) It was established that leaching with 5% H_2SO_4 removes more iron than with 10% H_2SO_4.

2) The chromium loss increases with increasing acid concentration.

3) Leaching at room temperature requires a duration of over 100 hours but leaching at 100°C can be completed in 3 hours.

4) The amount of iron removed by leaching at 55°C is comparable to that extracted at room temperatures. Leaching at 100°C removes an excessive amount of chromium.

5) During leaching iron dissolves at a higher initial rate than chromium. Quenching of hot briquettes is, therefore, suitable for the rapid leaching of iron without excessive dissolution of chromium.

6) Removal of iron from the chromite does not result in changes in the lattice parameters of chromite detectable by X-ray powder photography.

9.0 APPENDIX

1. Determination of Chromium and Iron in Chromite

Summary

This method of analysis is based on the fusion of finely ground chromite under alkaline oxidizing conditions. The fused product is leached in water, precipitating the iron in the form of hydrated ferric oxide. Quantitative separation of the iron from the chromium by filtration is hence possible, because the iron will report in the solid fraction and the chromium in the filtrate. The two elements can then be determined separately. The reactions in this process are as follows:

$$2FeCr_2O_4 + 7Na_2O_2 \longrightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O \quad (1)$$

$$NaFeO_2 + 2H_2O \longrightarrow NaOH + Fe(OH)_2\downarrow \quad (2)$$

For the analysis of chromium, the filtrate is acidified, converting the chromite into dichromate (see equation 3). The chromium content of the solution can then be determined by titrating against a ferrous ammonium sulphate solution of known concentration using N- methyldiphenylamine p- sulphonic acid as internal indicator. The titration reaction is shown in equation 4.

$$2CrO_4'' + 2H^+ \longrightarrow Cr_2O_7'' + H_2O \quad (3)$$

$$Cr_2O_7'' + 6Fe^{++} + 14H^+ \longrightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O \quad (4)$$

The ferric hydroxide is dissolved in hot hydrochloric acid and the ferric ions are then quantitatively reduced to the

divalent state by using a 25% stannous chloride solution. Any excess of reducing agent is destroyed with mercuric chloride. The ferrous ions are titrated with a standardised potassium dichromate solution using barium diphenyl sulphonate as internal indicator. The reactions occur in accordance with equations 5, 6 and 7.

$$2Fe^{+++} + Sn^{++} \longrightarrow 2Fe^{++} + Sn^{++++} \quad (5)$$

$$Sn^{++}(\text{excess}) + 2Hg^{++} \longrightarrow Sn^{++++} + 2Hg^{+} \quad (6)$$

$$6Fe^{++} + Cr_2O_7'' + 14H^{+} \longrightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O \quad (7)$$

PROCEDURE

Dissolution of Chromite

1. Approximately 1.0g of chromite is finely ground in an agate pestle and mortar.
2. The material is dried and 3 x 0.250 g are weighed accurately into 3 x 4cm diam., thickwall nickel crucibles.
3. 3g NaOH pellets and 5g Na_2O_2 are added to each crucible.
4. The contents are thoroughly mixed with a stout copper wire.
5. The crucibles are covered and are heated gently until the mixtures are melted.
6. The temperature is increased until the crucibles are dull red. This is maintained for about 20-30 min., swirling the crucibles frequently.
7. The crucibles and their contents are cooled and leached in 3 separate 600ml beakers with 100ml water.

8. The crucibles are removed and washed with distilled water.

9. 1.0g Na_2O_2 is added to each beaker. The solutions are boiled for 15 min.

10. The residues are separated by filtering through a No.541 Whatman filter paper. The filtrates are collected separately in 800 ml beakers

11. The residues are washed thoroughly with a hot, 1% Na_2CO_3 solution (approx. 150 ml of wash-solution is normally sufficient).

12. The filtrates can be used for the analysis of iron.

Chromium analysis.

1. 1:1 H_2SO_4 is added to the filtrate until the solution just turns yellow. Approximately 12 ml of acid is required. (If a precipitate is formed during this operation, an excess of acid is added until the precipitate redissolves.)

2. The solution is brought to the boiling point.

3. It is cooled and adjusted to 250 ml in a standard flask.

4. 100 ml of solution is pipetted into a 250 ml beaker.

5. 15 ml of solution alpha (150 ml conc. H_2SO_4 + 150 ml syrupy phosphoric acid diluted to one litre with distilled water) is added.

6. The solution is then titrated with a standard ferrous ammonium sulphate solution.

7. 4-5 drops of N- methyldiphenylamine p- sulponic acid indicator are added when the colour of the solution turns green. An intense reddish-purple colour will be developed.
8. The titration is continued until the solution becomes pure green. (When the end point is approached, the solution is stirred well, waiting for several seconds between each addition of the titrant).
9. The chromium content of the solution is then calculated.

Iron analysis.

1. The ferric hydroxide residue in the No.541 Whatman filter paper is dissolved in 15 ml of hot, conc. HCl in a 100 ml beaker. The filter paper is washed with a minimum amount of hot, conc. HCl. All washings are collected.
2. The solution is brought to the boiling point.
3. The solution is then removed from heating and 4-5 drops of 25% stannous chloride in 1 + 3 HCl is added dropwise (Excess stannous chloride is avoided).
4. 20 ml of saturated mercuric chloride solution is added. The solution is allowed to stand for 1 min.
5. 4 ml of conc. phosphoric acid is added.
6. This is followed by 3 drops of barium diphenylsulphate indicating solution.
7. The solution is titrated against standardised $K_2Cr_2O_7$ until the green solution becomes reddish-purple

8. The iron content in the solution can then be calculated.

Standardisation.

The standard ferrous ammonium sulphate solution for chromium determinations contains 20.000 g of dry crystals per litre acidified by 20 ml H_2SO_4. The standard potassium dichromate solution for iron determinations contains 0.400 g of crystals per litre. Both salts can be obtained in high purity and may be used as primary standards. They may be standardised against each other.

2. Determination of Chromium and Iron in Leach Liquor by Spectrophotometric Method.

Summary.

This method of analysis is based on the formation of stable ferric-E.D.T.A. and chromic-E.D.T.A. colour complexes under acid conditions. The ferric and chromic colour complexes possess absorption peaks at wavelengths below 366 mμ and at 538 mμ respectively. No interference between absorption peaks was experienced with solutions having concentrations of ferric and chromic ions of the same order of magnitude as those in the leach liquor. It is, therefore, possible to measure the absorption densities of the two colour complexes in one solution without separating the metal ions. The assay values of the iron and chromium can then be obtained by reference to calibration curves.

Development of Method.

Colour complexes.

The large number of analysis necessitated by this investigation justified the development of a rapid spectro-photometric method. It has been reported (99) that disodium ethylenediamine-tetra acetate forms a stable violet complex with chromic ion at boiling temperatures. The properties of this complex were studied by Cellini and Valiente (100) who observed two absorption peaks occurring at 396 mμ and 538 mμ, the latter being more prominent with a maximum value of absorption at pH 1.5-4.0.

Presence of chloride, nitrate, calcium, magnesium, aluminium and zinc ions did not interfere with the absorption peaks which remained stable up to 15 days.

E.D.T.A. also forms a stable yellow complex with ferric ions with an absorption peak at below 366 mμ and with an absorption density constant at a pH range of 0.8 - 2.8 (100).

Oxidation.

In qualitative analysis all iron and chromium ions in solution have to be converted completely into the trivalent state by controlled oxidation, avoiding the formation of ions in a more oxidised state e.g. dichromate. Different common oxidizing agents were investigated for their suitability in this application. It was found that oxidation by using KNO_3 and H_2O_2 resulted in having a solution with a lower concentration (approx. 10%) of chromic ion. Bromine water proved suitable and was used subsequently for this analytical process.

pH.

The range of pH values which could be employed in this analysis was studied for iron and chromium determinations. It was found that the pH value was not critical in the absorption measurements, provided it remained between 1.0 - 4.0. Sulphate ions were also found to have negligible effect on the determination at this pH range. Sodium carbonate and sulphuric acid were, therefore, used for pH adjustments in conjunction with a pH meter.

Interference

It was thought that interference between the absorption peaks of the two colour complexes may occur under the conditions of determination of the concentration of ferric and chromic ions. This aspect was investigated by studying the absorption densities of the colour complexes at different wavelengths. It was found that the absorption peak of chromic-E.D.T.A. complex in a glass cell occurred at 548 mμ and that of ferric-E.D.T.A. complex at below 329.5 mμ. For convenience a wavelength of 548 mμ was adopted for the determination of chromium and a wavelength of 329.5 mμ for iron determinations. Using 1.0 cm absorptiometric glass cells, solutions containing 2-20 mg iron/litre could be measured in a Unicam Spectrophotometer. For the measurement of chromic ions a solution of higher concentration was required. Sensitivity was between 20-200 mg of chromium/litre.

The concentrations of iron in the leach liquors were higher than that of the chromium and in view of the lower limits of iron concentration determinable by this method, the chromium was measured first, before diluting the solution for iron determination. No interference with the chromium absorption was detected under these conditions, nor was any interference of the iron reading by chromium observed after dilution. This procedure of determining two ions in one solution was, therefore, adopted for the analysis of leach liquors.

Procedure.

1. The leach-liquor is decanted from the leach-residue.
2. The residue is washed 3 times with small portions of 1% H_2SO_4. All washings are collected by decantation.
3. The leach liquor and the washings are combined together. The total volume is measured accurately.
4. An aliquor of 5 ml is pipetted from the solution.
5. This sample of solution is diluted 10 times in a 50 ml standard flask with water.
6. 10 ml of the diluted solution is pipetted from the 50 ml standard flask into a covered beaker.
7. 2 ml of saturated bromine water is added.
8. The solution is boiled vigorously for 5 min. to expel all the bromine.
9. The solution is cooled and is then neutralised carefully with Na_2CO_3 crystals to pH 2-3.
10. 5 ml of 5% E.D.T.A. solution is added to the solution
11. The solution is boiled gently for 5 min. in a covered beaker for complete development of colour complexes to occur.
12. It is cooled and made up to 20 ml with distilled water in a standard flask.

13. The optical density of the solution is measured at 548 mμ for chromium determination in 1 cm absorptiometric glass cell. The remaining solution is diluted and the optical density is then measured at 329.5 mμ for iron determination.

14. The iron and chromium content per litre of solution can be obtained by reference to calibration curves (see Figs. 20A and 20B).

15. The iron and chromium dissolved during leaching can be calculated.

Calibration.

Ferrous ammonium sulphate $[Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O]$ and chrome alum $[Cr_2(SO_4)_3.K_2SO_4.24H_2O]$ were used for obtaining calibration curves for the determination of chromium and iron. It was found that the optical density is directly proportional to the concentration:

$$D = mC$$

where D = optical density of solution in a 1 cm cell.

C = concentration of element in g/litre.

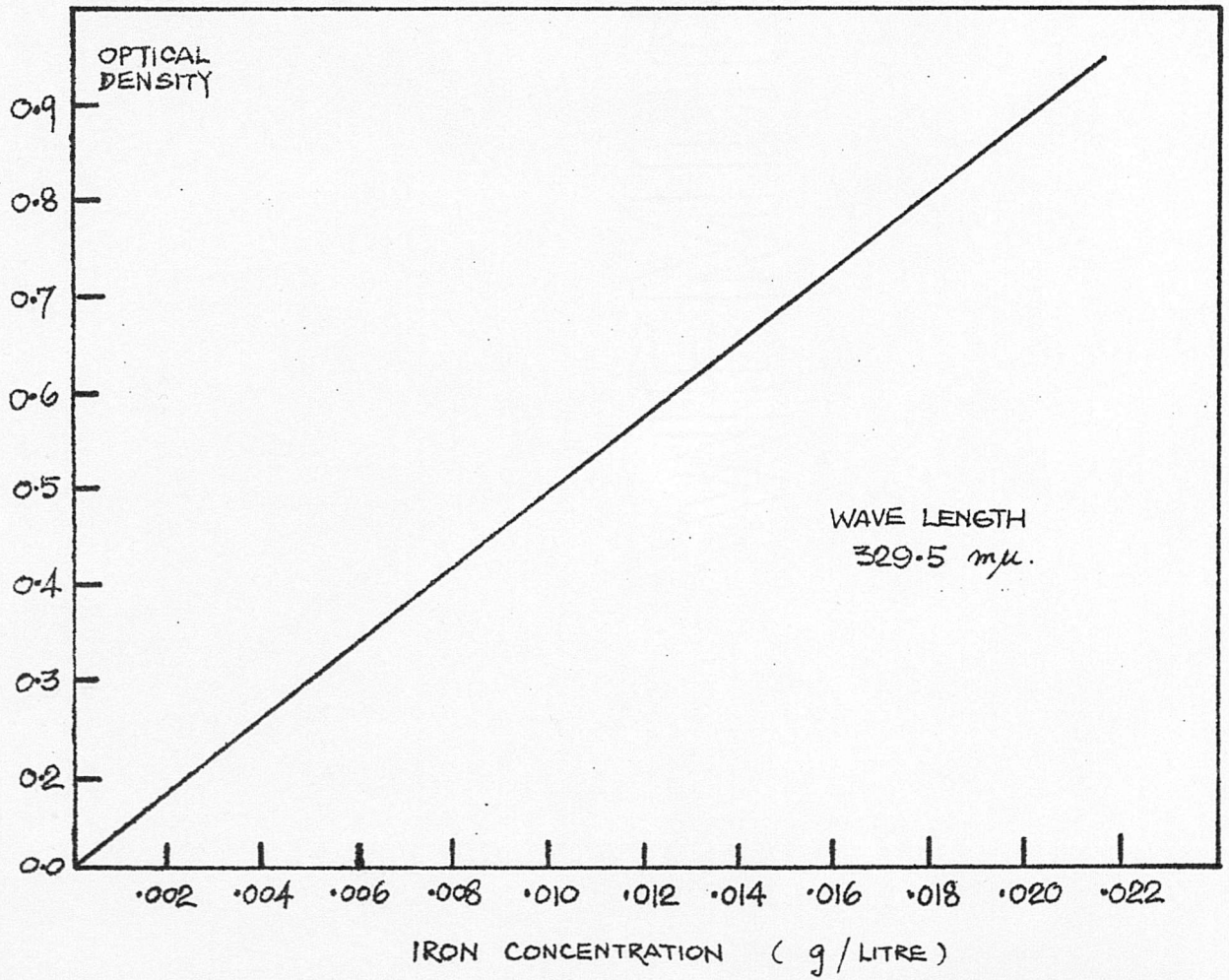
m = constant in units of optical density per gram/litre.

For chromium determination m = 3.65.

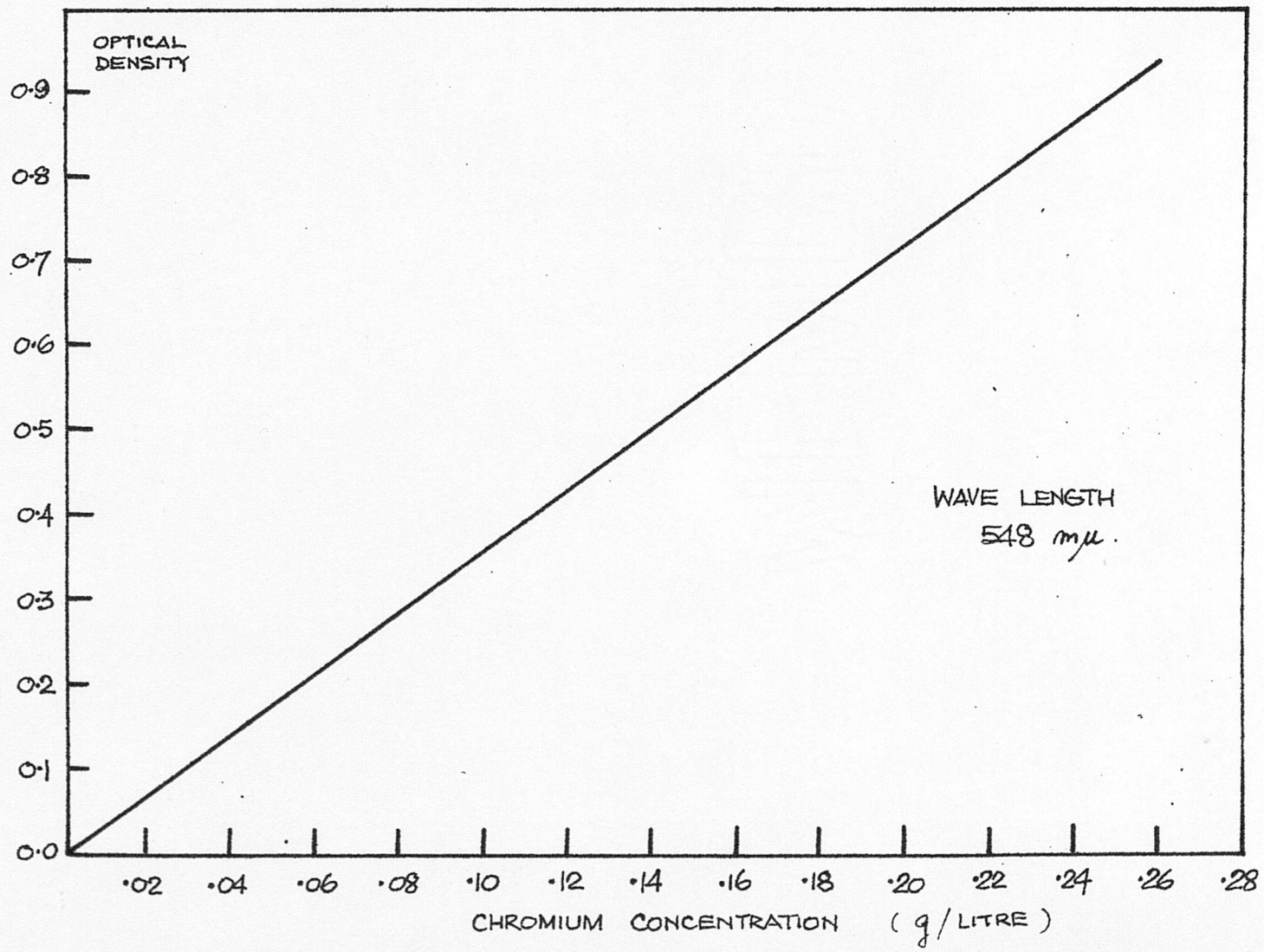
and for iron determination m = .463

The calibration curves of iron and chromium determinations are shown in Figs. 20A and 20B respectively.

CALIBRATION CURVE FOR IRON DETERMINATION FIG 20A



CALIBRATION CURVE FOR CHROMIUM DETERMINATION FIG 20B



10.0 BIBLIOGRAPHY

1. Iron Age : 132, 18, (1933).

2. Metal Progress : 23, 13, (1935).

3. Texter : Proc. Elec. Furn. A.I.M.M.E. 3, 133, (1945).

4. Udy : Metals and Alloys, 14, 52, (1941).

5. Macdonald : Metals and Alloys, 15, 249, (1942).

6. Metallurgical Laboratory, University of Melbourne : Investigation No.226, (1941).

7. Downes and Morgan : Department of Mines and Technical Surveys, Mines Branch, Ottawa, Canada, Memorandum Series No.116 (1951).

8. Farrow : Ph.D. Thesis, University of London, (1959).

9. Progress Report on Utilization of Bird River Chromite : Mines Branch, Ottawa, Canada, (1949).

10. Mines Branch, Ottawa, Canada, Investigation No.1492, (1943).

11. U.S. Bureau of Mines, Bulletin 436, (1942).

12. Aravanuthan and Srinivasan : Bulletin India Sec. Electrochemical Soc., 10, 67-68, (1961).

13. Boericke and Bangert : U.S. Bureau of Mines, R.I. 3817, (1945).

14. Lloyd et al : U.S. Bureau of Mines, R.I. 3834, (1946).

15. Misra, Sen and Bhatnagar : Trans. Indian Inst. of Metals, 12, (1959).

16. Sen and Chatterjee : Indian Mining Journal, Special Issue (1957).

17. Hammerberg : S. African Patent 739/36, (1936).

18. Boericke and Bangert : U.S. Bureau of Mines, R.I. 3813, (1945).

19. Boericke : U.S. Bureau of Mines, R.I. 3847, (1946).

20. Kubaschewski and Evans : "Metallurgical Thermochemistry", Butterworth Springer Ltd., London, (1951).

21. Andersson : French Patent 458,066, (1913).

22. Brackelsberg : U.S. Patent 1, 921, 114, (1933).

23. Barret : U.S. Bureau of Mines, R.I. 3229, 47, (1934).

24. Dean : U.S. Patent 2, 131, 006, (1936).

25. Ban : "Progress in Mineral Dressing", Stockholm, pg.365 (1958).

26. Hally and Apuli : "Agglomeration", Interscience Publishers, London, pg. 931., (1962).

27. Davies and Wade : University of Minnesota, Mines Expt. Station, Info. Circ. No.6, (1951).

28. Sterling : "Agglomeration", Interscience Publishers, London, pg. 177, (1962).

29. Donnan : Trans. Faraday Soc., 14, 12-13, (1919).

30. Firth : Blast Furnace, Coke Oven and Raw Material Committee, Iron and Steel Div., A.I.M.M.E., Proc. 4, 46, (1944).

31. Tigerschoild and Ilmoni : Blast Furnace, Coke Oven and Raw Material Committee, Iron and Steel Div., A.I.M.M.E., Proc. 9, 18, (1950).

32. Drake : Ind. Chem. Eng., 41, 780, (1949).

33. Haines : J. Agri. Sci., 17, 264, (1927) and 20, 97, (1930).

34. Fisher : J. Agri. Sci. 16, 492, (1926).

35. Newitt and Conway-Jones : Trans. Inst. Chem. Engr. 36, No.6, (1958).

36. Haines : J. Agri. Sci., 15, 529, (1925).

37. Cooke and Ban : Chem. Eng. Prog., 55, 364, (1955).

38. Hardesty and Chucka : Chem. Eng. 60, 116, (1953).

39. Swartzman : Canadian Mining and Met. Bulletin, 57, No.505318, (1954).

40. Cooke and Stowasser : Trans. A.I.M.E., 193, 1223, (1952).

41. Ban and Erk : Trans. A.I.M.E., 196, 803, (1953).

43. Ridgion, Cohen and Lang : Journal Iron and Steel Inst., London, 177, 43, (1954).

44. Cohen, E. : Royal School of Mines, London, Private Communication, (1961).

45. Urich and Han : "Agglomeration", Interscience Publishers, London, pg.669, (1962).

46. Jewitt, Wood and Hansen : U.S. Bureau of Mines, R.I. 5762, (1961).

47. Stevenson and Bergstrom : Mining Eng., April, 1962.

48. Tigerschoild : J. Iron and Steel Inst., London, 177, 13, (1954).

49. Reynolds : Phil. Mag., 20, 469, (1885).

50. Sherwin and Stevenson : Soc. Chem. Ind., London, Chem. Eng. Group, Proc., 31, 1, (1949).

51. Cooke and Ban : Trans. A.I.M.E., 193, 1053, (1952).

52. Merklin and DeVaney : Mining Eng. Journal, March, (1960).

53. Violetta : Mining Eng., March, pg.354-364, (1958).

54. English and Morgan : Mining Eng., March, pg. 354-364 (1958).

55. Kurt, Meyer and Rausch : Mining Eng., March, pg. 354-364 (1958).

56. Sewerynski and Wlazinska : Prac. Inst. Ministerstwa Hutnic, 7, 30-34, (1955); C.A. 1955, 12237b.

57. Cohen, E. : J. Iron and Steel Inst., London, 175, 160.

58. Smrcek, Rericha and Kandl : Hutnicke Listy, 16, 318-324 (1961).

59. DeVaney : Mining Eng., March, pg. 354-364, (1958).

60. Ban : "Progress in Mineral Dressing", Stockholm, pg. 365, (1958).

61. Winchell and Winchell : "Elements of Optical Mineralogy" Wiley, (1951)

62. Geld and Esin : Doklady Akad. Nauk., S.S.S.R., 73, 541-544, (1950).

63. Bockris, Kitchener and Davies : Trans. Far. Soc., 48, 536, (1952).

64. Boericke : U.S. Bureau of Mines, R.I. 3747, (1944).

65. Pokorny : C.A., 52, 19785a.

66. Glasstone : "Text Book of Physical Chemistry", MacMillan and Co. Ltd., pg. 1029/1030, (1957).

67. Moleva and Kasakin : Stal., 12, 1068-1070, (1957).

68. Hamaker: Physica, 4, 1058, (1937).

69. London : Trans. Faraday Soc., 33, 8, (1937).

70. Rumpf : "Agglomeration", Interscience Publishers, London, pg. 379, (1962)

71. Jones : "Fundamental Principles of Powder Metallurgy", Arnold, London, pg. 387, (1960).

72. Thomas, D.L. : Royal School of Mines, London, Private Communication, (1958).

73. Rhines, Birchenall and Hughes : Trans. Am. Inst. Mining Met. Engrs., 188, 378-388 (1950).

74. Geach and Jones : Research, 2, 493-494, (1949).

75. Alexandra and Balluffi : Acta. Met., 5, (11), 666-677, (1957)

76. Kuczynski : Acta Met., 4, (1), 58-61, (1956).

77. Bockstiegel : J. Metals, 8, (5), 580-585, (1956).

78. Clark and White : Trans. Brit. Ceram. Soc., 49, 305-329 (1949/1950).

79. Navias : J. Am. Ceram. Soc., 39, 141-145, (1956).

80. Iida and Ozaki : J. Am. Ceram. Soc., 42, 219-228, (1959).,

81. Chaklader and Roberts : Nature, 183, 1252-1253, (1959).

82. Moser and Whitmore : J. Appl. Phys., 31, 488-493, (1960).

83. Holowaty, Goldfein and Sheets : Proc. A.I.M.E., Blast Furnace, Coke Oven and Raw Material, 14, 43, (1955).

84. Wild and Dixon : "Agglomeration", Interscience Publishers, London, pg. 565, (1961).

85. Voice, Wild and Skalla : British Iron and Steel Research Association, Research Investigation No.IM/S/29/56, (1956).

86. Wild and Burgess : British Iron and Steel Research Association, Research Investigation No. IM/S/27/59, (1959).

87. Wild and Oldroyd : British Iron and Steel Research Association, Research Investigation No. IM/AA/27/55, and IM/AA/57/55, (1955).

88. Davis and Mitchell : "Progress in Mineral Dressing", Stockholm, pg. 305 (1958).

89. Limons and Kraner : "Agglomeration", Interscience Publishers, London, pg. 117, (1962).

90. Rovenskii : Iron and Coal Trade Review, March, (1960).

91. Wild : J. Iron and Steel Inst., 174, 135 (1953)

92. Krotkiewski and Sewerynski : Prac. Inst. Ministerstwa Hutnictwa, 7, 101, (1955), c.f. Brutcher, No. 3707.

93. Lang and Carveth : Proc. 2nd Biennial Coal Briquetting Conf. Info. Circ. No.5, Univ. of Wyoming (1951).

94. Tonry : "Agglomeration", Interscience Publishers, London, pg. 1, (1962).

95. Cohen and Schloegl "Progress in Mineral Dressing", Stockholm, (1958).

96. Treadwell and Hall : "Analytical Chemistry" Vol. 1, John Wiley and Sons, (1916).

97. Evans : "Crystal Chemistry", Cambridge, (1939).

98. Derbyshire : Thesis, 1958, Universal Microfilm, M.I.C. 58, 1773.

99. Welcher : "The Analytical Uses of Ethylenediaminotetra acetic Acid", D. Van Nostrand, (1958).

100. Cellini and Valiente : Anales Real Soc. Espan. fis. y. Quim. (Madrid), 51B, 47-52 (1955); C.A. 48, 11973, (1955).