THE EXTERNAL DESULPHURISATION
OF HOT METAL

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June, 1980

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SUMMARY

This thesis is based on works trials and laboratory model studies.

Iron samples taken on the works showed that a sample from the torpedo gave an adequate estimate of the iron sulphur level.

The mixing characteristics of iron during the calcium carbide based torpedo injection process were examined using a model. The modelling criterion was that the energy input per unit mass of liquid should be the same for the model and the plant. The mixing time was primarily dependent on the lance immersion depth and the rate at which the gas evolving agent was introduced to the iron. The effect on the process of torpedo internal skulls was demonstrated. The results of this model work were confirmed by plant data, and were used in making adjustments to the operation of the plant.

A torpedo model was used to study the effects of its mouth shape on desulphurisation slag removal. The most significant factor was the metal pouring rate but the mouth shape determined the ease of removing the large lumps of slag which occur.

A works trial was carried out injecting soda ash as a flux with the calcium carbide mixture at the desulphurisation plant. The data indicated that some internal skull prevention took place.

A transfer ladle model was used to demonstrate the effectiveness of gas bubbling as an aid to carbide desulphurisation slag removal.

This model was used to determine the iron mixing characteristics for the transfer ladle injection desulphurisation process. It was found that the plant operating conditions maximised the mixing of iron in the ladle. Changes predicted by the model were supported by plant results.

This work has shown the usefulness of the application of model results to large scale plant operation.

Key Words: Iron
Desulphurisation
Modelling
Torpedo
Transfer Ladle

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SYNOPSIS

The last few years have seen increasing demands from steel users for higher quality products. In most cases this has meant a reduction in the steel sulphur level. Meeting this demand, coupled with the need to minimise processing costs in the face of increasing sulphur contents in ironmaking raw materials, has confirmed the external desulphurisation of iron as an integral part of the Blast Furnace - B.O.S. production route.

Many methods of external desulphurisation are available. The most common being based on calcium carbide as the desulphurant, using mechanical stirring or injection to make contact between the carbide and the molten iron. At the Scunthorpe Works of the British Steel Corporation, (B.S.C.), calcium carbide mixed with calcium carbonate is injected into 200t. torpedo ladles (cylindrical ladles c. 1.7 x 12 m (internally) used for the transport and temporary storage of iron, or into 275t. transfer ladles (open top ladles c. 3.6 m. mean diameter).

In order to optimise torpedo plant operation a number of trials were required. These necessitated an accurate knowledge of the pre-treatment sulphur level. The best estimate of this analysis was obtained by accurately scheduled multiple sampling from the blast furnace runner. However, if this was not possible the homogeneity of iron in the torpedo under most filling conditions meant that the errors involved in taking a single immersion sample from the torpedo before treatment were acceptable.

One of the major factors influencing the efficiency of desulphurisation in a torpedo is the ability of the process to stir the iron, bringing the sulphur into the reaction zone. The calcium carbonate is added as a stirring agent. On contact with the molten iron it decomposes and the gas evolved produces turbulence as it rises through the metal. Experiments using a perspex/water model have illustrated the flow patterns set up in a torpedo during injection. The model has enabled some quantification of the effects of material injection rate, lance angle and immersion depth, and torpedo internal skulls, on metal mixing times. Process efficiency is optimised by using the maximum lance immersion depth at a point as close as possible to the centre of the torpedo. The degree of mixing is increased by increasing the proportion of carbonate in the reagent. However, above a critical value, which depends on the shape of the torpedo no further benefit is obtained.

The slag formed in the torpedo during the desulphurisation process, under Appleby-Frodingham operating conditions, resulted in skull formation and a reduction in iron carrying capacity. Trial results showed that the rate of skull/slag build up could be reduced by the addition of soda ash to the carbide mixture. However the quantity added, 10%, was insufficient to remove the skull or increase slag fluidity so that it could be poured from the torpedo. Soda ash should only be used on plant which has good fume collection and cleaning facilities.

The flow of slag from the torpedo was examined using a water model. It was shown that removal was aided by fast pouring through a wide rectangular mouth.

The effort of iron desulphurisation is wasted if the high sulphur slag formed is charged, with the iron, to the steelmaking vessel. It is standard practice at the Appleby-Frodingham Works to skim this slag from the transfer ladle using a mechanical rabble. Gas bubbling at the back of the ladle was known to enhance the removal of solid magnesium slags by skimming. Water model tests showed that the technique was equally applicable to carbide slags and significant benefits to operation were demonstrated.

The transfer ladle injection system was also studied using the water modelling technique. It was shown that the operating conditions used on the plant maximised the mixing rate of iron in the ladle. Increases in the mixing potential of the system did not significantly reduce the measured homogenisation time.

The performance of the transfer ladle process is less dependent than the torpedo process on the mixing characteristics of the system. Improvements in performance are most likely to be obtained by replacing solid calcium by a liquid or gaseous reactant.

1. INTRODUCTION

The world market for steel is making increasingly stringent quality demands on its suppliers, who in turn are striving to minimise their overall processing costs. One of the major areas of concern is the final steel sulphur level. It is important because of its direct relationship to reject levels during processing, especially with respect to surface finish and cracking. It is significant in defining steel properties especially when considering brittle fracture, fabrication and welding. In general terms, it is above 0.030/0.025%S that quality and productivity are most sensitive to sulphur content, however for many applications, levels much lower than this are required.

The manufacturing units at the Appleby-Frodingham Works of British Steel's Scunthorpe Division are typical of a modern integrated plant: 3 x 300 t. B.O.S. vessels served by hot metal from blast furnaces. The major products are rod, plate and sections. The future aim of the plant is to produce all its steel at less than 0.030%S.

The sulphur removal capacity of the B.O.S. vessel is limited, therefore steel sulphur level is dependent on the blast furnace hot metal available. It is very expensive to produce iron at the low sulphur levels required to give the desired content in the steel. Therefore, external means of desulphurising the iron are used, and it is on this process that productivity and quality performance depends.

The aim of this thesis is to review the need for low sulphur levels in iron and the means of achieving them, and to examine the processes in use at the Appleby-Frodingham Works and the problems involved in their operation.

2. LITERATURE REVIEW

2.1. Sulphur and Steel Quality

Cracking and surface defects usually appear during the primary rolling of ingots and on the product of continuous casting machines. The steel must then be dressed before further processing can take place. Cracks are formed because the solidified shell of steel formed during casting cannot support the stresses set up during its contraction. A major reason for this weakness in killed steel is the formation of type II stringer sulphides, which precipitate between the growing dendrites and reduce the ductility of the steel just below the solidus. This is particularly so if they occur at grain boundaries where a crack may propagate. From the binary phase diagram it can be predicted that liquidous iron sulphides will not form in low carbon low manganese steels at sulphur levels less than 0.01% at the temperatures of hot working and heat treatment and will not therefore give rise to hot shortness.

The most susceptible grades are Al killed steels containing 0.18 - 0.22% carbon where the peritectic reaction occurs with a sudden volume contraction.

Data for silicon killed and rimmed steel ingots has been presented (ref.1) and is reproduced in Figs. 1, 2, 3, showing the effects of sulphur level on cracking and dressing frequency, and gives an indication of the higher teeming rates possible with reduced steel sulphur levels.

EFFECT OF SULPHUR CONTENT ON SLAB CRACKING - KILLED STEEL

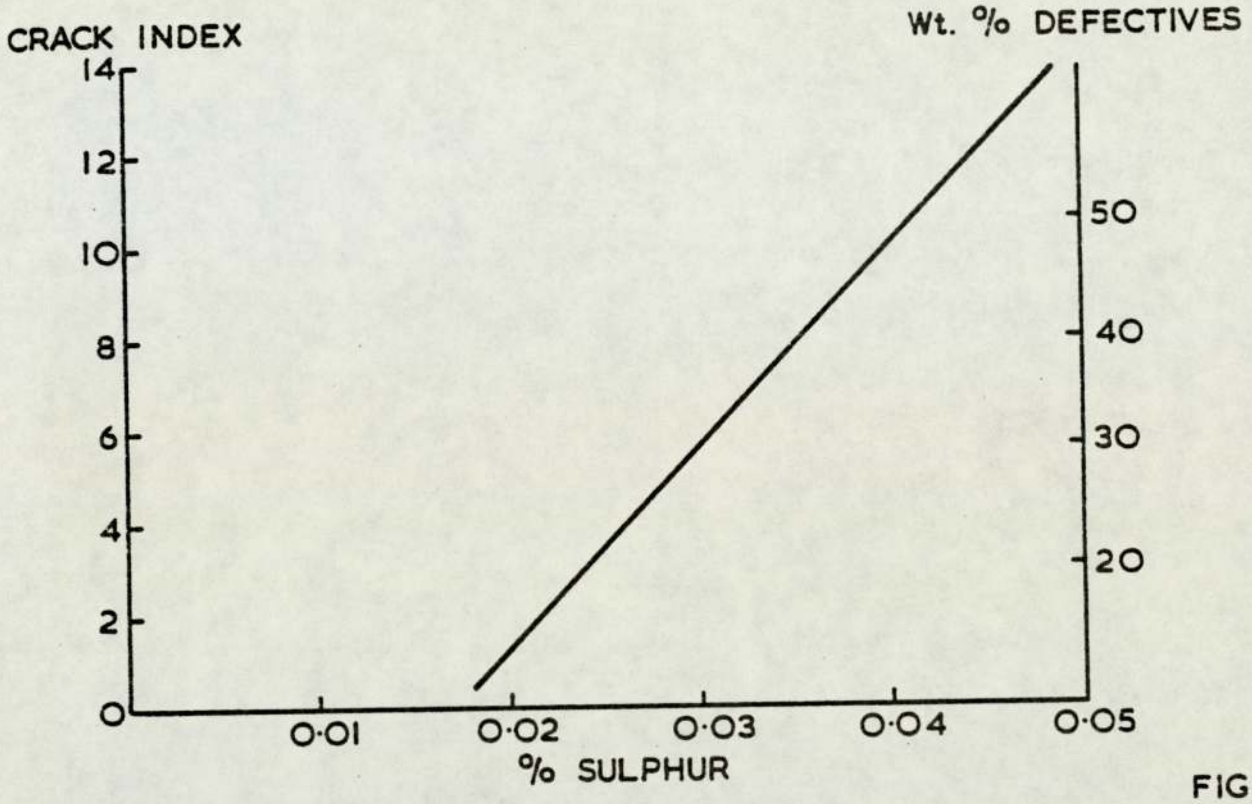


FIG 1

EFFECT OF TEEMING RATE ON SLAB CRACKING - KILLED STEEL

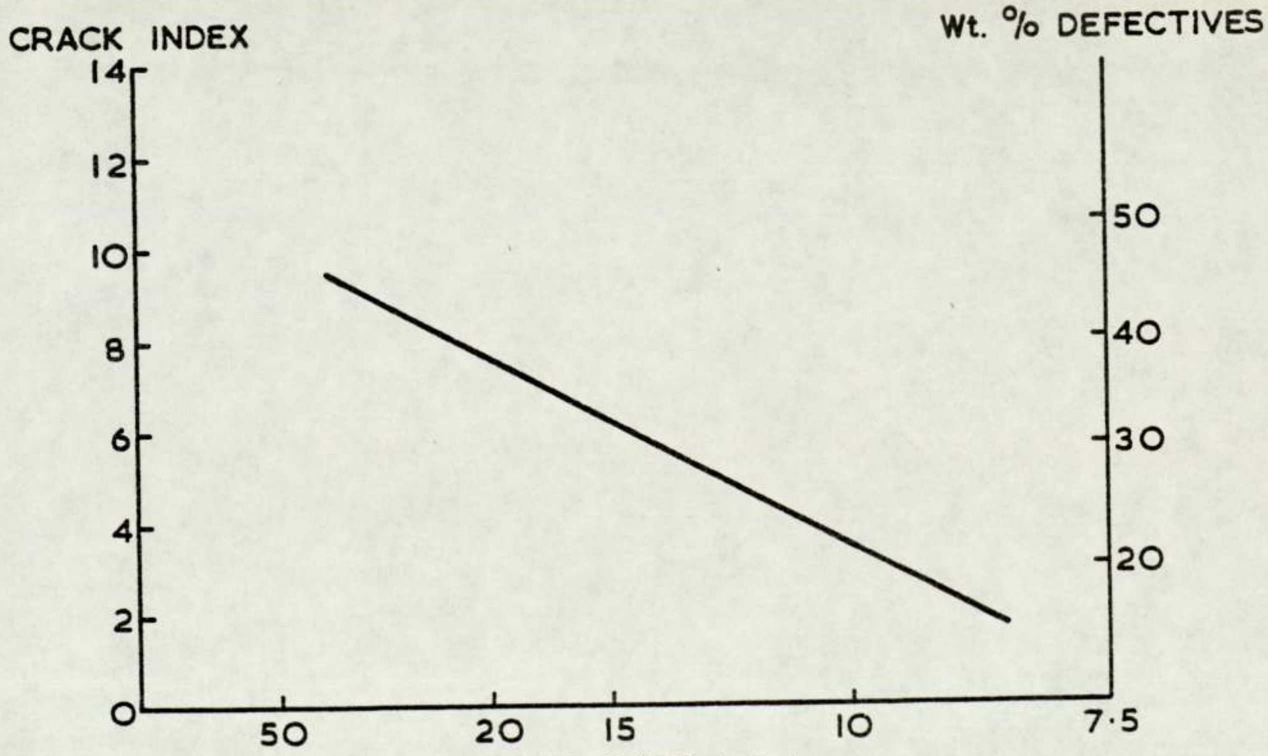
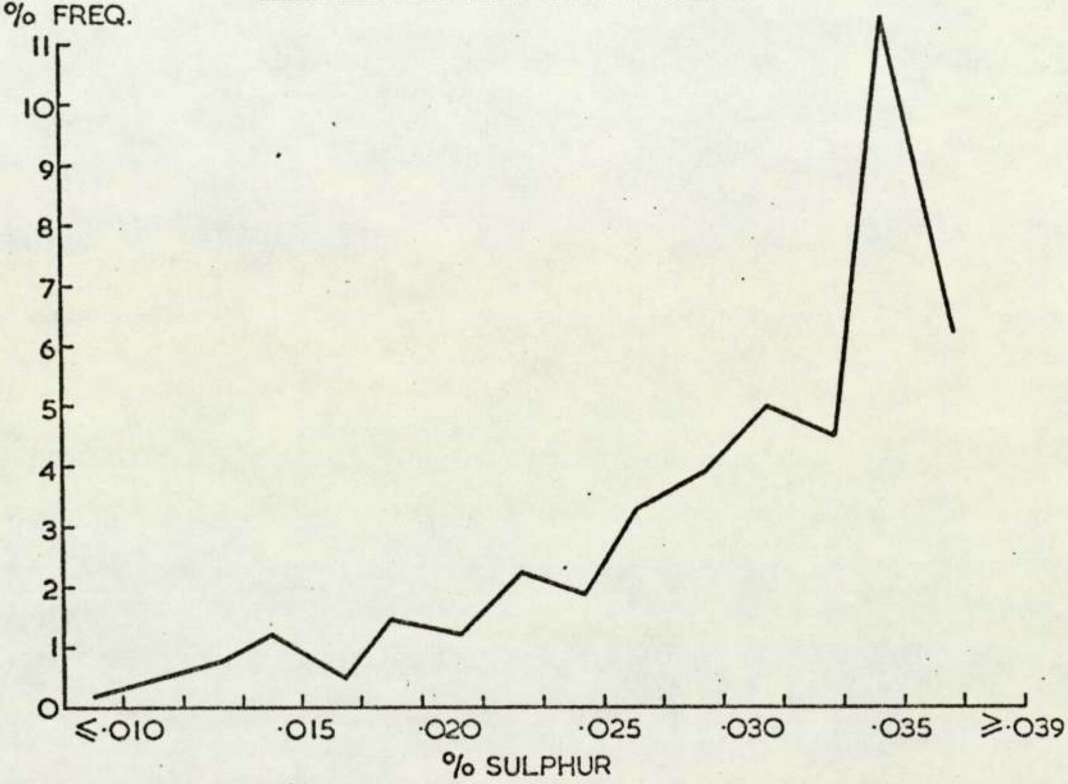
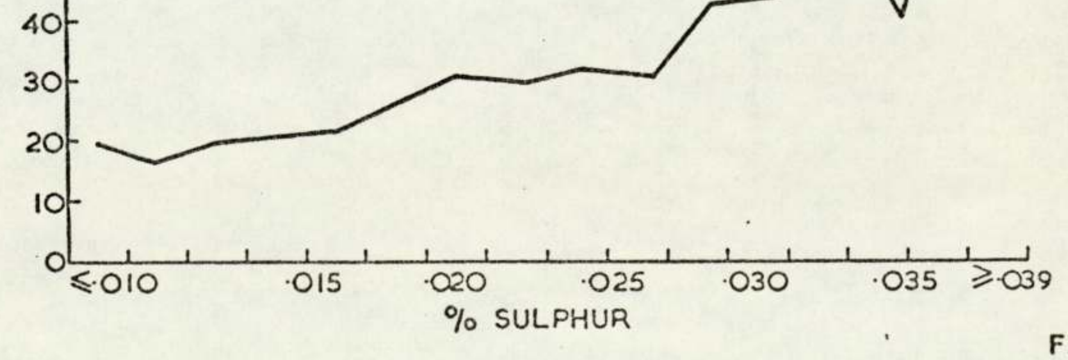


FIG 2

EFFECT OF SULPHUR CONTENT ON EDGE AND SURFACE DRESSING OF SLABS - RIMMING STEEL



SLABS BOGIE BURNED FOR EDGES



SLABS 70 - 100% AREA DRESSED

FIG 3

Continuous casting has a higher potential yield than the traditional ingot route and demands better surface quality to obtain this yield. The cooling rates and stresses however are higher, particularly in the case of slabs, as produced at the Appleby-Frodingham Works plant, and the sulphur levels therefore have to be reduced. The majority of plants operate at less than 0.025%S, but it has been shown that less than 0.020%S is required to minimise slab defects, and this is the level aimed for and achieved at Appleby-Frodingham, Fig.4.

There is in general a trend toward lower sulphur levels for all steel products, the future aim for the Appleby-Frodingham plant is to bring 100% of steel production to less than 0.030%.

Probably the most important criteria in steel product use are the resistance to brittle fracture, the formability, and the weldability. Normal structural steels have minimum Charpy energy values of 27 and 41 Joules in longitudinal samples for low and high strength steels respectively. These properties are achievable with 0.04%S steels. Where conditions of high stress and extreme cold occur extra limits of failure resistance are asked for. Typical examples are the North Sea drilling rig applications where Charpy energy values are specified at 61 J minimum at - 20°C longitudinally, and 27 J, minimum at - 50°C longitudinally and transversely with sulphur levels of 0.015% maximum.

Resistance to brittle fracture is increased as the steel sulphur is reduced. A 0.01% decrease in sulphur increases the Charpy shelf energy by 20 J, Fig.5. This increase is because of the presence of fewer type II sulphides which become elongated during rolling and form planes of weakness along which a crack may propagate. Reductions in sulphur level reduce this problem by decreasing the number and extent of the sulphides. The sulphides themselves can be modified using such elements as Cerium and Zirconium, (ref. 1, 2, 3), the undeformable sulphides formed almost doubling the energy at any particular sulphur level. The sulphur content however, still retains its effect on the energy level.

A tearing potential exists when stresses occur through the plate thickness beneath a weld which are not relieved because of the rigidity of the total framework. Typical examples are oil node plates (the welding of several large diameter thick walled pipes), fillet welding, and pressure vessel nozzles. Often the most suitable steels for these applications are those which are fully killed with aluminium, which are the most susceptible to stringer type manganese sulphide inclusions. Susceptibility to tearing is normally measured by the reduction of the area (R.A.) of a tensile test piece machined in the transverse direction. The greater the R.A. value, the greater the resistance to tearing, its variation with sulphur level is shown in Fig. 6. Values of 5 to 15 meet normal standards but for special applications as for node plate R.A.'s of 35% minimum average and 20% minimum individual are required plus Charpy V-notch values of 27 J at - 50°C in the transverse direction. These can be reached by sulphur levels of 0.010% maximum in Si killed Al grain refined steels up to 75 mm. thick.

DISTRIBUTION OF SLAB SULPHUR LEVELS
APPLEBY-FRODINGHAM

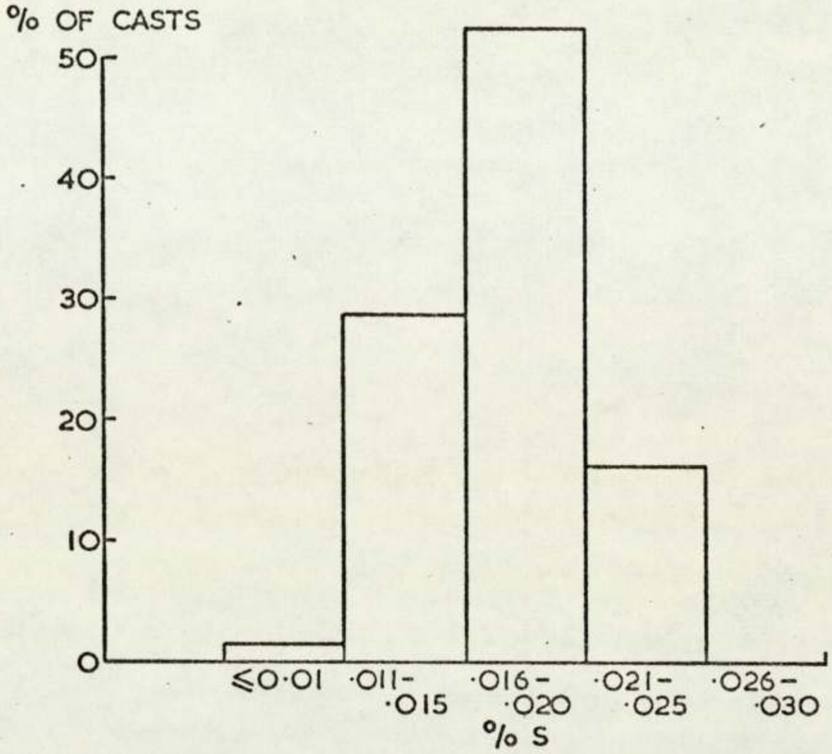


FIG 4

EFFECT OF SULPHUR CONTENT ON CHARPY SHELF
ENERGY - CONTROLLED ROLLED STEEL

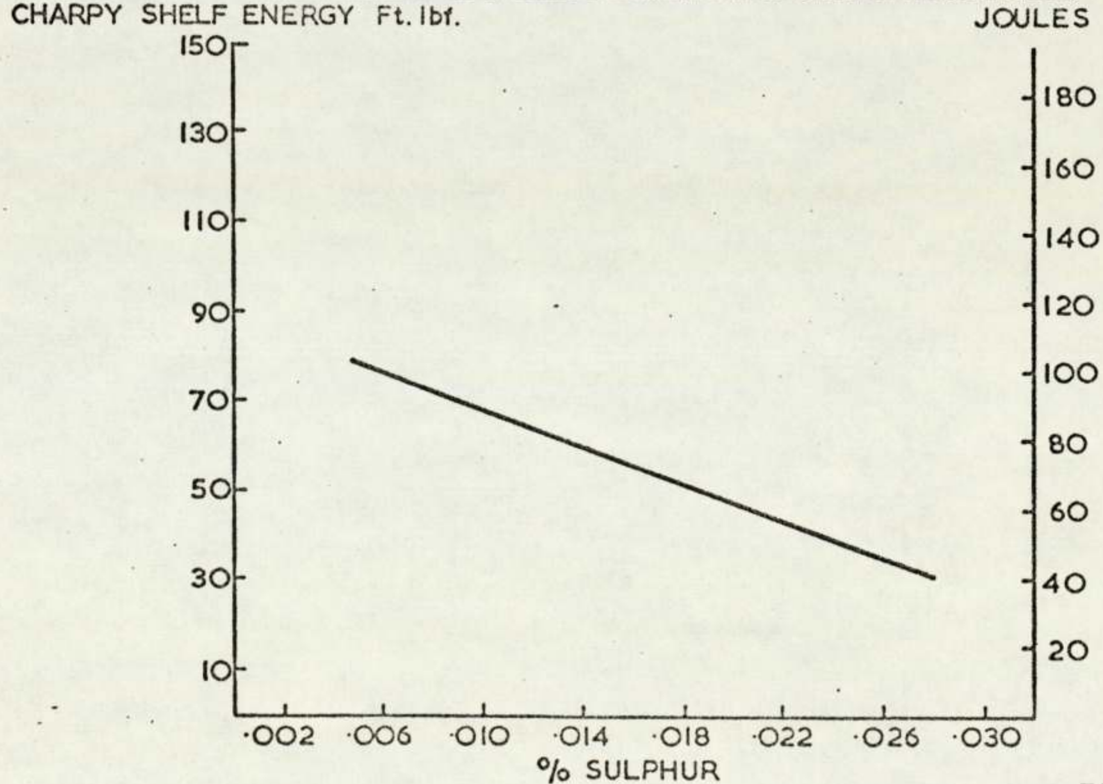


FIG 5

A large proportion of steel undergoes welding during fabrication and the sulphur level is one factor which affects cracking and tearing in the joint area. Cracks occur by the formation of low melting point high sulphur eutectics which are relatively weak and crack under the stresses of solidification, although carbon content does play a vital role. A more severe form of cracking is in the parent plate, by liquefaction of manganese sulphides in the heated area. The former has greatly been controlled by control of sulphur level in welding rods, using basic fluxes and coated electrodes and reducing the plate sulphur level to minimise dilution effects. The latter can be controlled by reducing heat input to the weld but this is not generally desirable and the reduction of plate sulphur levels is the best answer. It must be remembered that modern welding techniques are fast with high heat inputs to achieve the necessary production rates.

Lamellar tearing is the tearing of the metal in a direction parallel to its plane surface and can extend for several feet. Again its presence is associated with stringer sulphide inclusions. The through-thickness strength of materials is becoming increasingly important.

The importance of sulphur level when shaping steel has been recognised for some time. Steels which are to be only lightly worked may have sulphur levels of 0.03 - 0.04% but for more severe pressing applications with cold reduced rimming steels 0.025% or in some cases 0.015% will be required. Tests have shown (ref. 1.) that gains in formability can be made with improving cleanness in higher strength steels.

Some of the quality constraints specified do not apply at present to the normal Appleby-Frodingham Works products. However many steel mills are selling material of quality far in excess of customer demands. It is therefore important for the plant to have the flexibility to be able to match this market demand.

The sulphur content of steel is important not only because of its effect on product quality but also because of its influence on processing and costs in the steelplant and rolling mills. For the processing route at Appleby-Frodingham Works substantial savings and benefits will accrue from achievement of the 0.030%S maximum. (This topic has been the subject of a thorough study by the department in which the author works - results and data are not published.)

2.2 Sulphur and Iron and Steel Production at Appleby-Frodingham

Having established the need for steels with low sulphur contents one must examine the methods of production available. The normal production route for large scale operations is the refining of iron, produced by a blast furnace, in a B.O.S. vessel, as in the Appleby-Frodingham Works process route. It is the interaction of both possible and best practice between these two units that creates the need for an independent method for reducing the sulphur content of the system.

Blast furnace operation demands the use of large quantities of coke. A simple balance shows that this coke is responsible for 84% of the sulphur load, Fig. 7. Coke sulphur contents are controlled by the sulphur level in the coal blends. Pricing policy and transport costs dictate that the bulk of the coal blends must be from the closest mining area. Of the major ironmaking centres Scunthorpe coal sulphurs are the highest, resulting in high sulphur coke, Fig. 8.

The other major blast furnace feed is sinter. The sinter making process uses coke as a fuel. However during sintering a considerable removal of sulphur can be obtained. This depends upon the basicity of the sinter produced. By changing the blend of ore, coke and fluxes the proportion of sulphur transferred to the sinter can vary from 10% to 70% at basicities of 0.2 and 4.0 respectively (basicity = $CaO + MgO/SiO_2 + Al_2O_3$), in the latter case the sinter retains the fuel sulphur in the form of stable solid compounds. At Appleby-Frodingham Works, a self-fluxing sinter is produced and practically all the sulphur in the fuels is removed in the fume.

EFFECT OF SULPHUR CONTENT ON SHORT TRANVERSE REDUCTION OF AREA (R.A.)

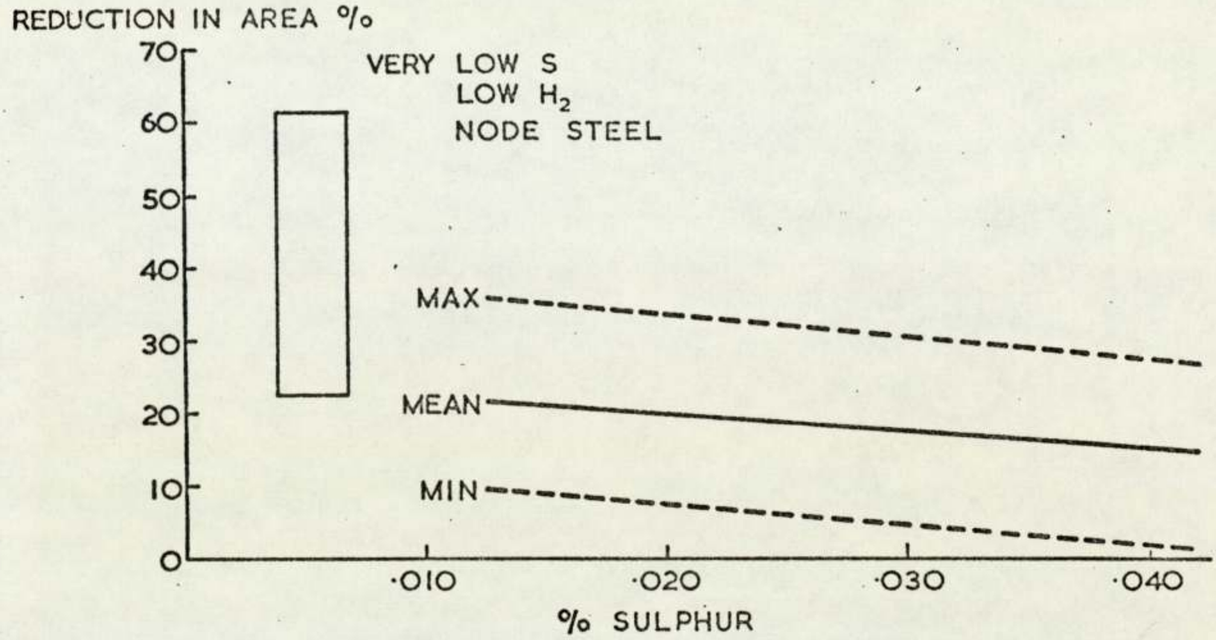


FIG 6

SIMPLIFIED BLAST FURNACE SULPHUR BALANCE APPLEBY - FRODINGHAM

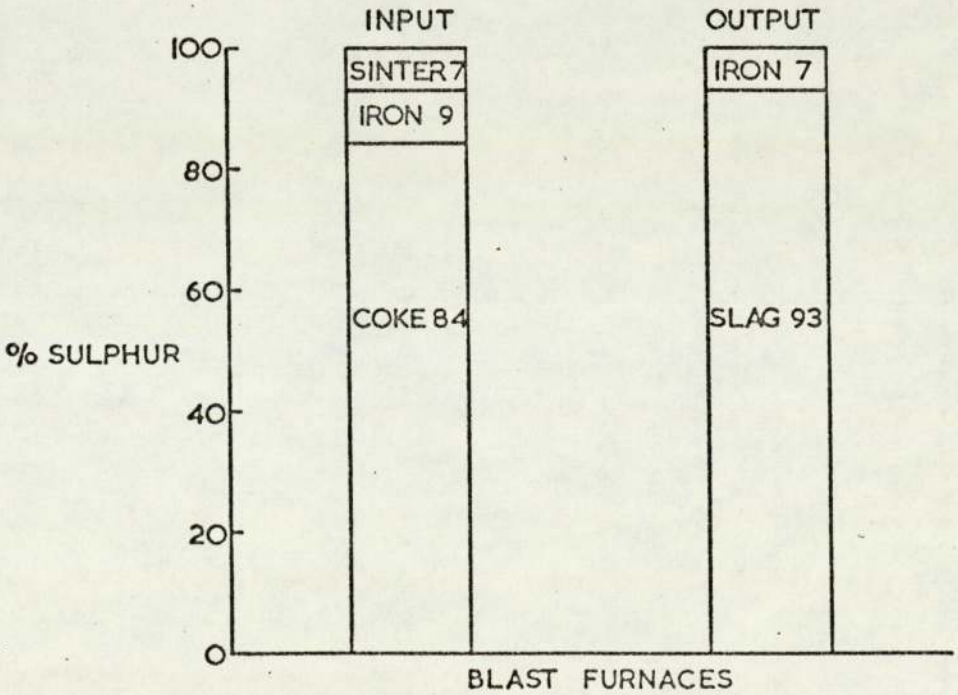


FIG 7

The blast furnace itself is an extremely efficient sulphur removal unit only some 5 to 7% remaining in the metal. This efficiency is because of the strongly reducing conditions in the bosh and hearth and the increase in activity of the sulphur caused by the carbon and silicon present in the iron. Sulphur input with the coke and hence output with the iron can be reduced by using coals with a low sulphur level but these in the case of Appleby-Frodingham Works would have to be imported and could significantly increase the final iron cost.

In the furnace itself the amount of sulphur taken up by the slag can be increased by increasing the sulphur partition $\frac{(S)}{[S]}$ coefficient and/or by increasing the slag volume. The partition coefficient is mainly dependent on the slag composition expressed as basicity, for otherwise constant iron composition. Increased slag basicity results in increased slag/metal sulphur partitions and hence lower iron sulphurs, Fig. 9. On a rich ore practice the basicity can be increased by increasing the limestone addition to the sinter plant feed, but at Appleby-Frodingham Works, which uses a proportion of local calcareous ore the quantity of this ore may be increased. The latter of course is the cheapest method but production rate suffers.

Increases in slag volume for given sulphur partitions and basicity obviously increase the quantity of sulphur leaving the furnace in the slag, and are affected by the same methods used to increase basicity. Fig.10.

COAL & COKE SULPHURS FOR THE MAJOR IRONMAKING CENTRES

AREA	% S	
	COAL	COKE
SCOTLAND	0·75	0·60
SOUTH WALES	1·00	0·80
TEESIDE	1·30	1·10
SCUNTHORPE	1·50	1·20

FIG 8

RELATIONSHIP BETWEEN SULPHUR PARTITION AND COMPLEX SLAG BASICITY

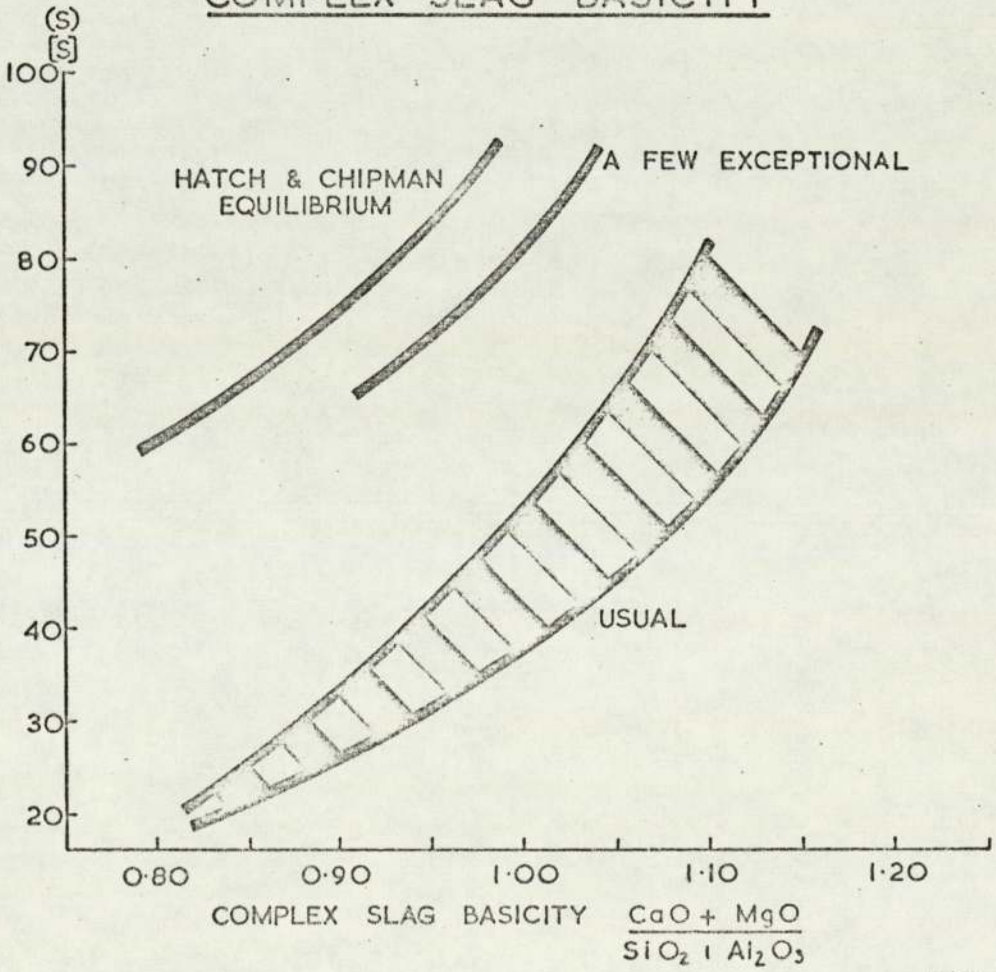
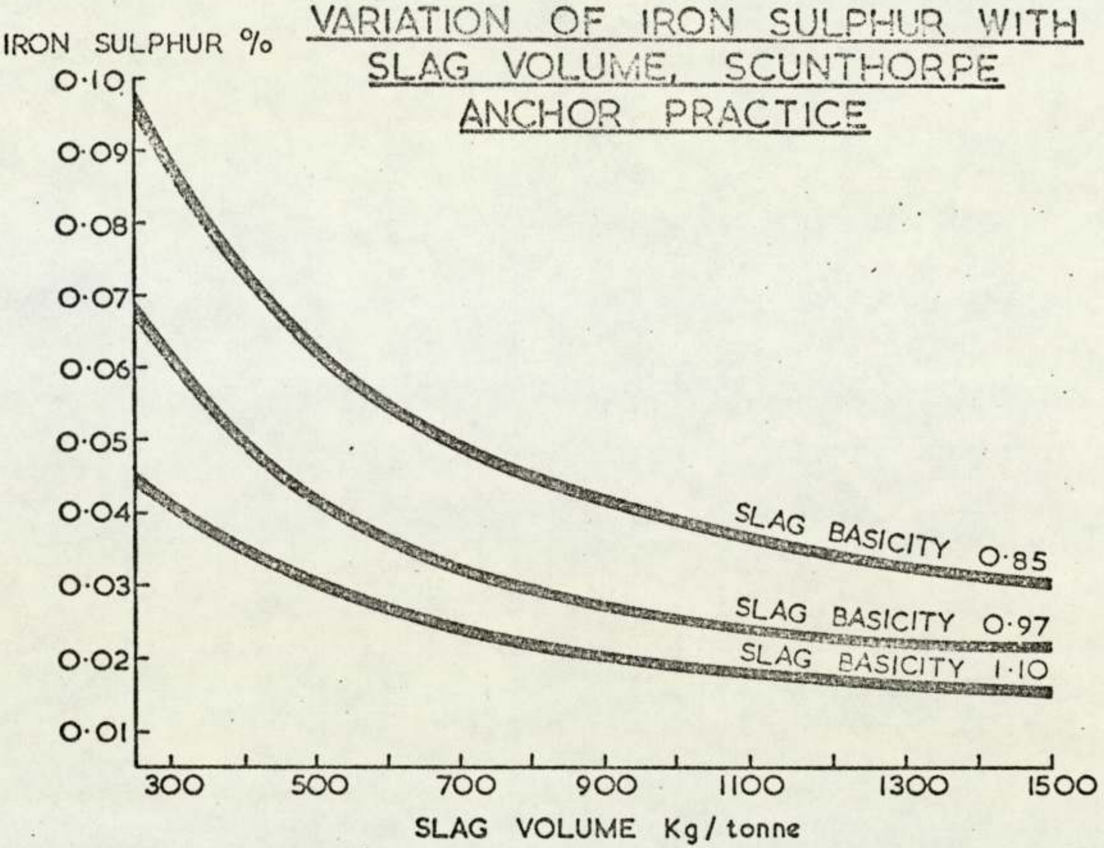


FIG 9

All the means of reducing iron sulphur content can be costed. All furnaces have a sulphur level which gives minimum working slag volume and maximum output. Obtaining sulphur levels below this starts to increase cost. The furnaces at Appleby-Frodingham Works could operate at sulphur levels of 0.075% to 0.10% at coke sulphurs of 0.6% to 1.2% with no nominal cost increase occurring. The cost increases (at 1973 prices) for producing low sulphur iron on a rich ore practice are given in Fig. 11. The sudden increase occurs at the basicity limit and lower sulphur levels can only be obtained by increases in slag volume. This type of curve tends to be very specific to one plant but will exist for all, in a similar form. As a general rule if the furnace has to process more coke or burden to reduce iron sulphur level then output will decrease.

Therefore the situation is that to produce iron sulphur levels of less than 0.035% the blast furnaces at Appleby-Frodingham face rapid escalation of costs coupled with reduced output rates. The problems of the steelmaker are further increased because to allow for the wide variations about the aim which occur in blast furnace operation, the normal target sulphur level is 0.050%.

The iron is refined in B.O.S. vessels for which a typical sulphur balance is given in Fig. 12 (ref. 5). The process removes about 50% of the sulphur input into the final slag, only a small proportion leaving with the waste gases, (ref. 5).



VARIATION OF IRON SULPHUR WITH SLAG VOLUME, SCUNTHORPE ANCHOR PRACTICE

FIG 10

INCREASED COST FOR THE MANUFACTURE OF LOW SULPHUR IRON, RICH ORE PRACTICE

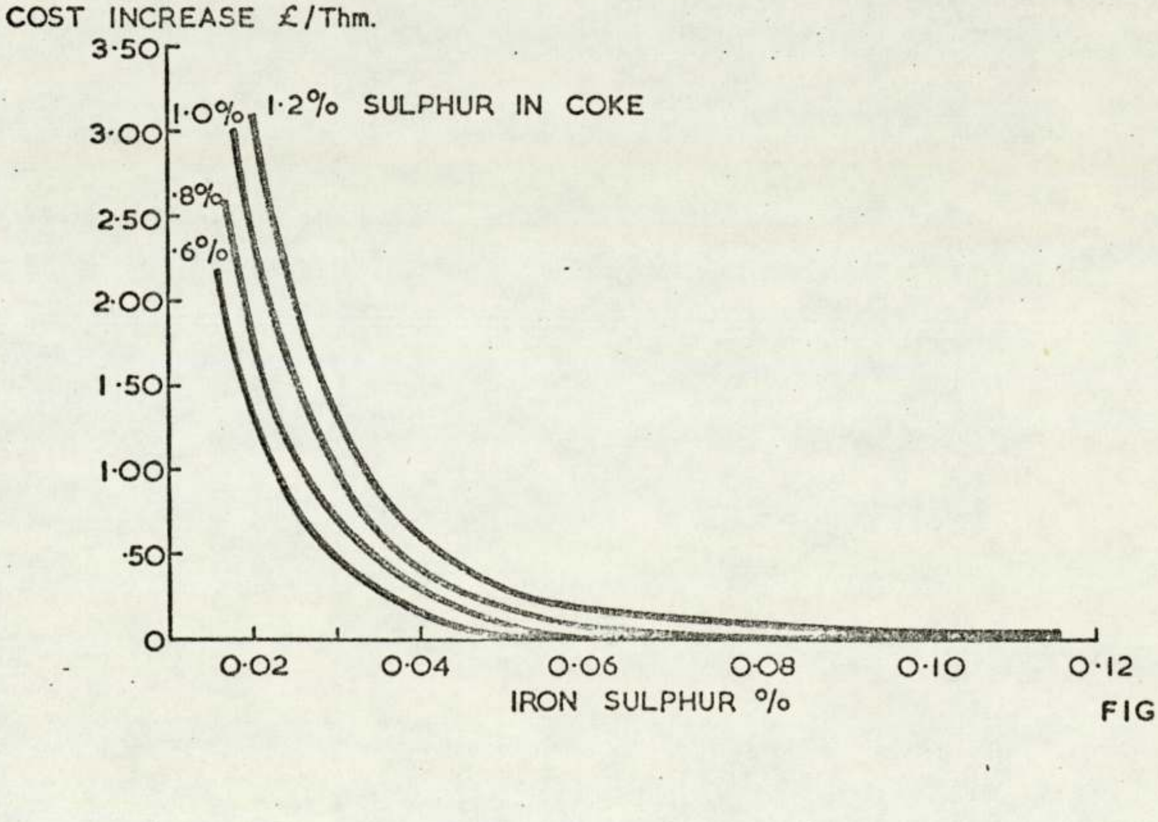


FIG 11

TYPICAL B.O.S. SULPHUR BALANCE

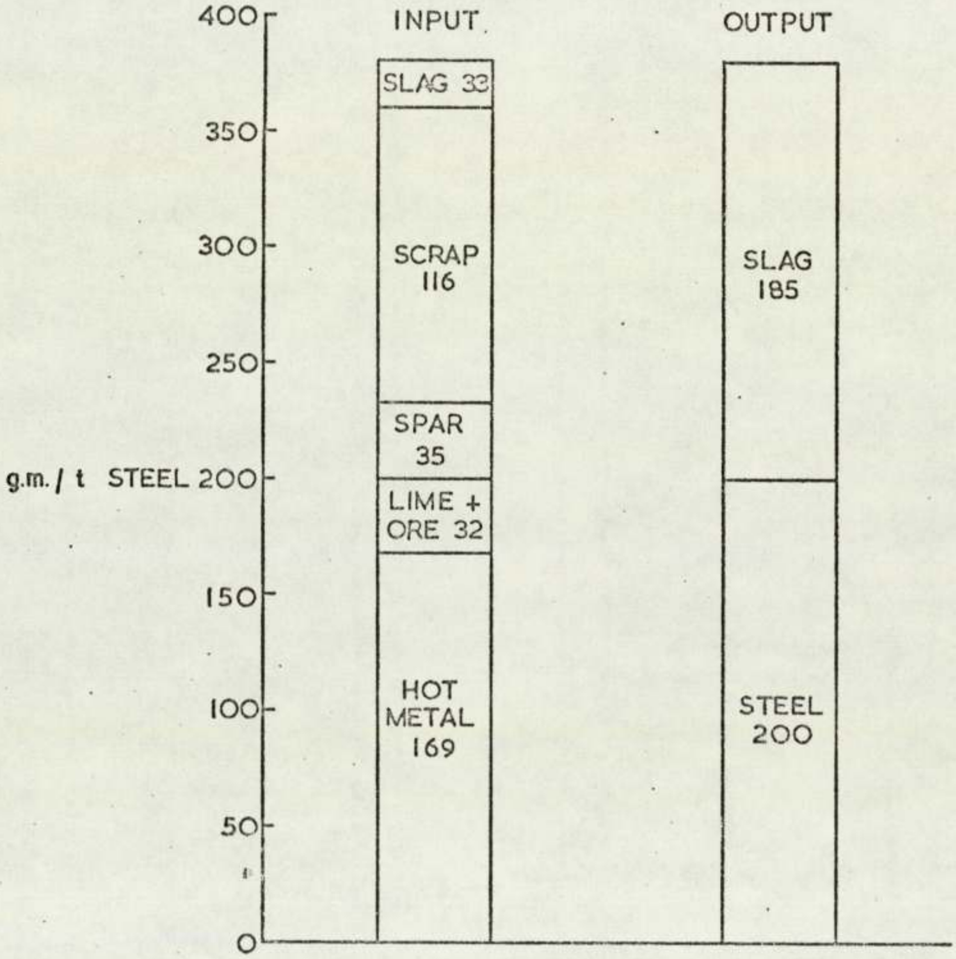


FIG 12

The sulphur partition coefficient between slag and metal can vary from about 4 to 10 depending upon action taken whilst refining the steel, its effect being illustrated by the data in Table 1. It is obvious that control of input material sulphur levels, excluding hot metal from the blast furnaces, can substantially reduce the steel sulphur content. Works trials recently conducted have quantified the effects of the above, (ref. 6).

Liquid slags in contact with liquid iron can be represented by the reaction,

$$\underline{S} \text{ metal} + O^{--} \text{ slag} = S^{--} \text{ slag} + \underline{O} \text{ metal}$$

and $$K_S = \frac{a_{S^{--}} \cdot a_{\underline{O}}}{a_{\underline{S}} \cdot a_{O^{--}}}$$

Oxygen ions are produced by the basic components of the slag CaO, MgO, MnO and decreased by reaction with the acid components. The sulphur reaction therefore depends upon the excess or free oxygen ion concentration as measured by the slag basicity. The basicity used in this work is defined as:

$$B = \frac{\% \text{ CaO} + 1.4 \times \% \text{ MgO}}{1.86 \times \% \text{ SiO}_2 + 1.18 \times \% \text{ P}_2\text{O}_5}$$

where % CaO is total % CaO - % free CaO.

TABLE 1

Effect of Sulphur Partition on Steel Sulphur Levels

$\frac{(S)}{[S]}$	% S steel
5	.0276
6	.0254
7	.0235
8	.0219
9	.0205
10	.0193
11	.0182
12	.0172

Total sulphur load 383 Kg., slag wt. 45 t.
steel wt. 300 t.

As more lime goes into solution in the slag the rise in O^{2-} will cause sulphur to be transferred from the metal to the slag, i.e. $\frac{(\% S)}{[\% S]}$ will increase. Increases in the oxygen content of the metal should inhibit sulphur transfer to the slag or even cause reversion. This does not normally occur in B.O.S. practice even with low carbon steels and high slag FeO contents. The increase in slag FeO produces a more fluid slag and increases lime solubility, the resulting increase in basicity and CaO in solution in slag for reaction more than outweighs changes in oxygen potential. The trial results shown in Fig. 13 indicate a larger than expected increase in $\frac{(S)}{[S]}$ with basicity.

This was attributable to the change in the physical condition of the slags observed. As the basicity increased there was a change from thick, through intermediate, to fluid slags. All the slags were in a heterogeneous area, as given by a modified CaO - SiO_2 - FeO diagram, Fig. 14, (ref. 7), even at the maximum temperatures, containing both liquid slag, solid dicalcium silicate and possibly tricalcium silicate, and unreacted lime. Only the liquid slag was available for reaction with sulphur since the solid phases absorb sulphur to a much smaller extent. The thick slags were further from the 1620°C isotherm than the fluid slags and therefore contain large proportions of the solid phases. Increased lime additions for sulphur removal, and repeated blowing of heats is then only of benefit if the lime can be brought into solution in the slag. This is only possible to a limited extent.

SULPHUR PARTITION VS. SLAG BASICITY

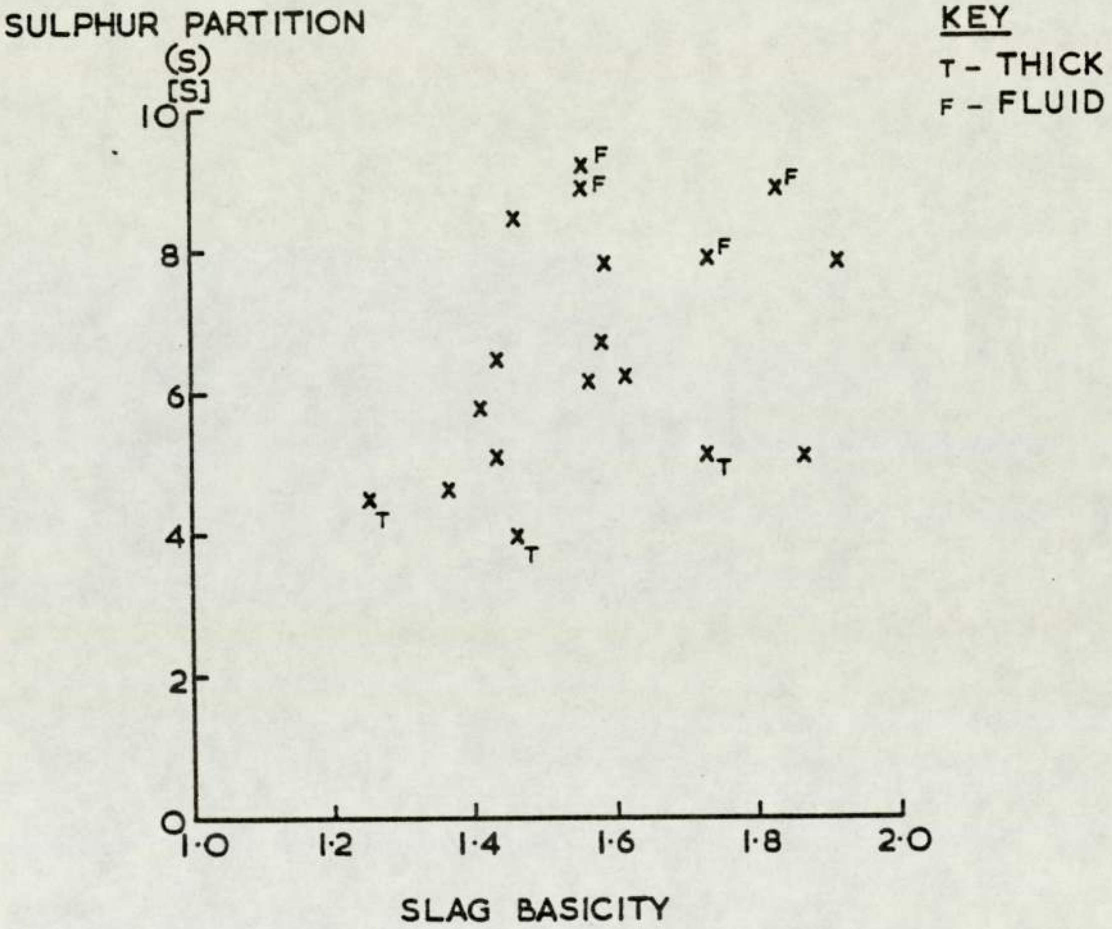
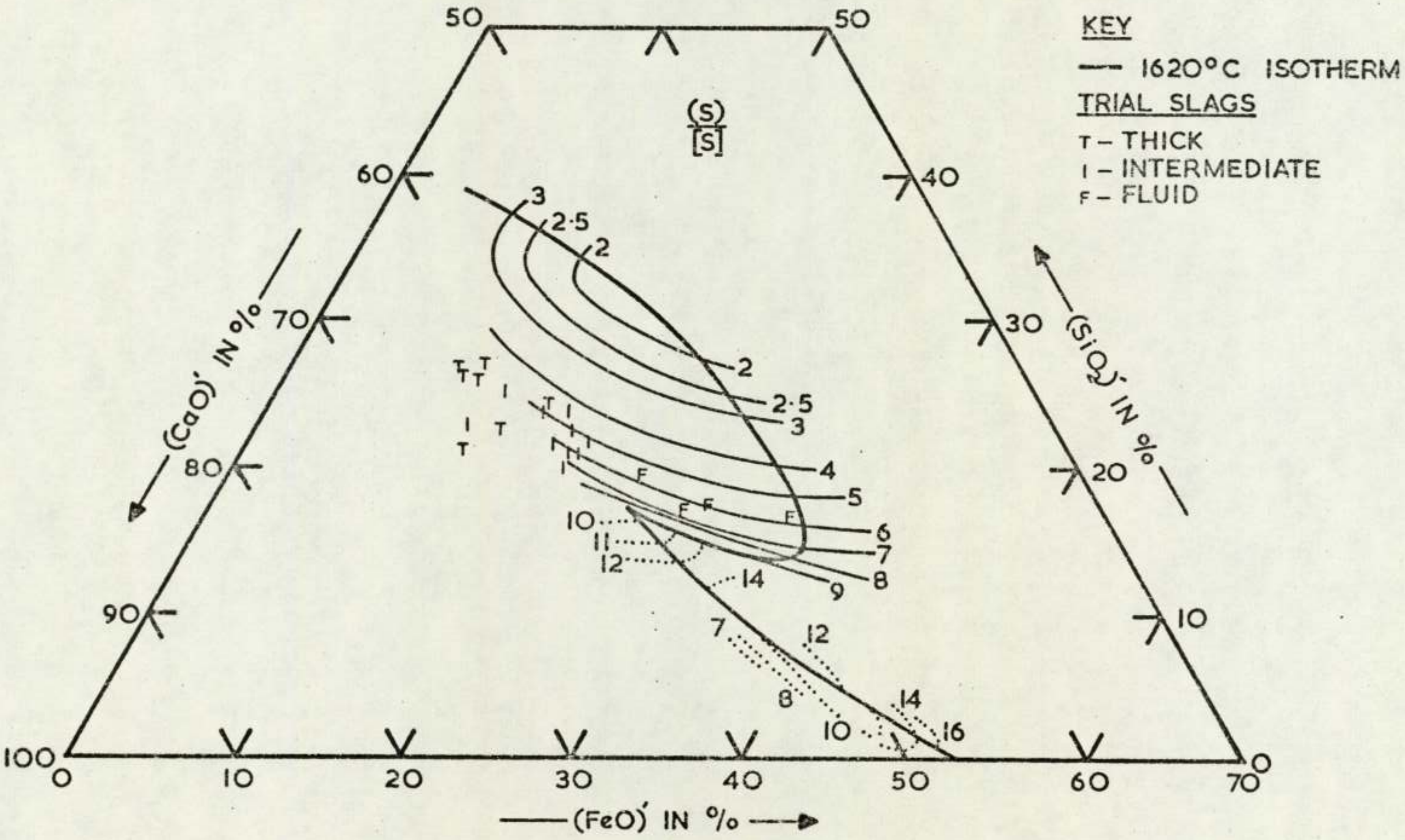


FIG 13

LINES OF EQUAL SULPHUR PARTITION IN THE $(CaO)'-(SiO_2)'-(FeO)'$ SYSTEM AT 1620°C



AVERAGE SLAG COMPOSITION $CaO + SiO_2 + FeO = 80\%$

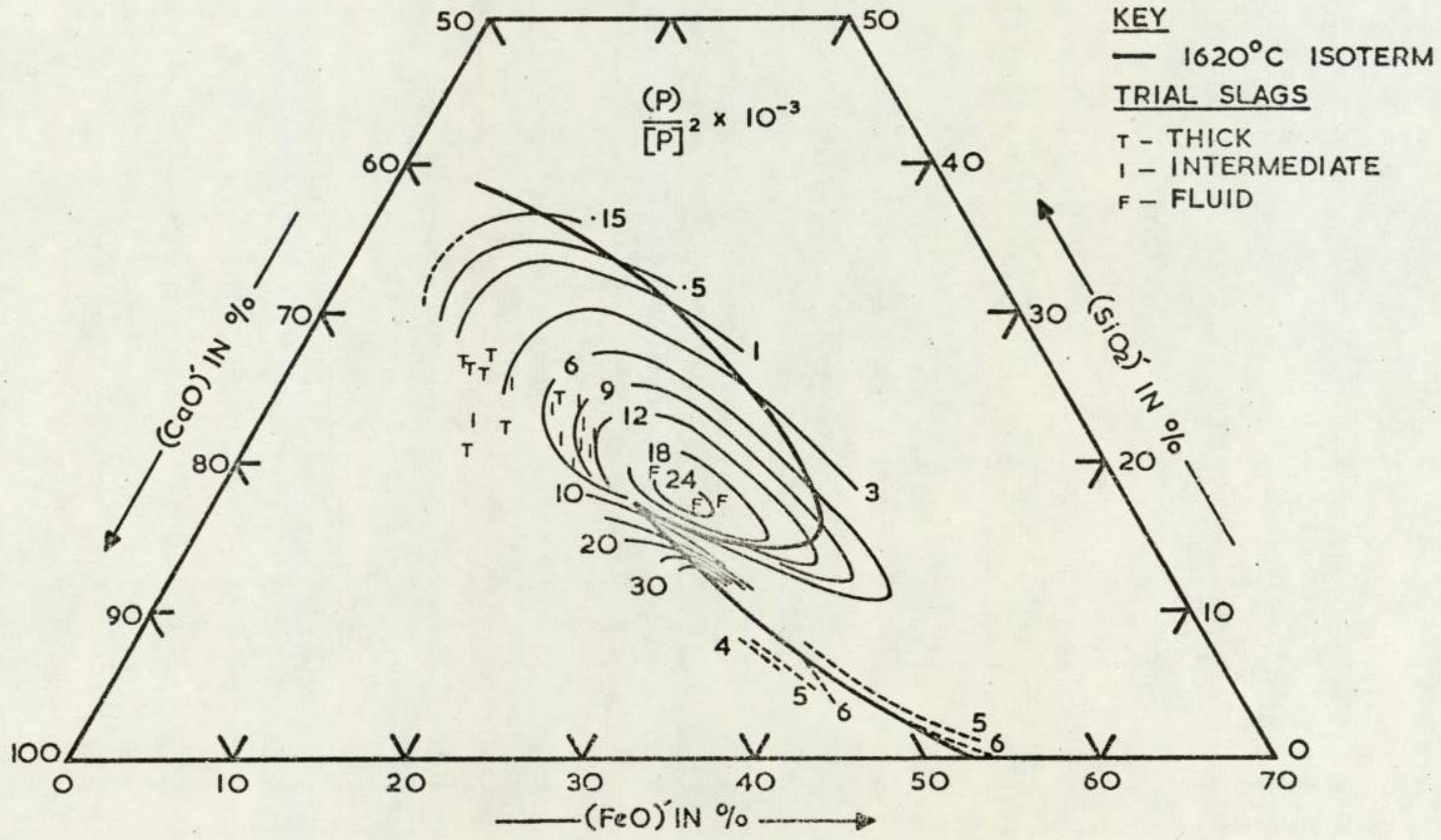
FIG 14

It should be noted that in the search for increased sulphur partitions in the vessel the phosphorus partition can be adversely affected, Fig. 15. Large changes in $\frac{(S)}{[S]}$ can be made for relatively little benefit, it must of course be maximised for low sulphur levels but the greatest benefits are obtained by limiting sulphur input to the vessel.

For normal steel sulphur levels and normal charge mix the contribution of sulphur from fluorspar and lime is not large, Fig. 12. However when low sulphur iron is being refined for low sulphur steel the contribution becomes significant and must be controlled. The major variables are the scrap and the hot metal and its accompanying slag. Scrap sulphur level is difficult to control on a cast by cast basis if a plant is aiming for a low overall steel sulphur level, but is easier to control for individual casts of low sulphur steel out of a normally higher range. The slag on the iron charged to the furnace can be reduced to about 0.5% of the metal weight by skimming or using tapholes in the metal transfer vessels. This is of increased importance if the metal has been desulphurised.

The major means of steel sulphur control is therefore through the hot metal. However the demands of the steelmaker cannot easily or economically be met by the ironmaker, the link between the two is the external desulphurisation of the iron.

LINES OF EQUAL PHOSPHORUS PARTITION IN THE $(CaO)'-(SiO_2)'-(FeO)'$ SYSTEM AT 1620°C



AVERAGE SLAG COMPOSITION $CaO + SiO_2 + FeO = 80\%$

FIG 15

2.3. External Desulphurisation

2.3.1. Introduction

A few years ago the majority of external desulphurisation was carried out using soda ash, applied as a batch to the steelmaking vessel charging ladle or to an intermediate ladle in the melting shop. As the demand for lower and lower sulphur iron has grown, the deficiencies in this method, in accurate prediction of end points, excessive fume, difficulty of handling large quantities, have made the steelmaker look to more predictable, more efficient processes. The most common first choice of material was lime because of its availability and price. Unfortunately, lime by itself is a relatively inefficient desulphuriser and today desulphurising reagents are normally based on more reactive materials such as calcium carbide and calcium cyanamide, (ref. 8-16). The methods of application vary with the conditions pertaining at a particular plant but are of two basic forms, addition by injection, and addition to a stirred ladle. Single reagents tend not to be used, and the desulphuriser is mixed with a material intended to increase the reaction efficiency by increasing the mixing of the metal bath and/or by inducing conditions that promote the desulphurisation reaction. Tables 2 and 3 list the most common reagents and methods of application. The general methods will be described first followed by a comparison of the variants and their operating results.

TABLE 2

Calcium Based Desulphurants

1. CaC_2
2. $CaC_2/CaCO_3$ 75/25/80/20
3. $CaCN_2/CaCO_3$
4. CaO/Na_2CO_3
5. CaO
6. $CaO = CaC_2/CaCO_3/C$
7. CaO, Propane/N_2
8. $CaO/CaC_2/Na_2CO_3$
9. CaC_2/CaO
10. NaOH with and without CaC_2/CaO
11. $CaCN_2$, $CaCN_2/CaCO_3/C$
12. Perrin slag Process (CaO, Al_2O_3, SiO_2 MgO) - as slag
13. CaO/C
14. (11) + 0.2% SiO_2 amorphous

TABLE 3

Desulphurisation Methods Employed

(with materials reference (Table 2)

	Method	Material
1.	Injection	1, 11, 2, 3, 5, 6, 7, 8, 9, 4, 14.
2.	Solid stirrer	1, 4, 9, 5, 13.
	Hollow stirrer	1, 4.
	Eccentric stirrer	1.
3.	Continuous Vessel Injection	
	- up current	1.
	- Down current	1.
4.	Shaking Ladle	5.
5.	(Continuous) Rotary Reactor - pilot scale for B.F. use	10.
6.	Agitation by gas injection (CTIF/Volianik process)	1.
7.	CaO based slags	12.
8.	(Siphon Ladle as 3)	

2.3.2. Soda Ash Treatment

The traditional limitations of soda ash treatment have been outlined above, however its reliability can be improved by several methods.

The simplest of these is to reladle the iron after the first treatment. This action remixes the metal and slag, and can increase desulphurisation by up to 30%. However the extra ladle handling and increased problems of ladle wear and maintenance make the practice incompatible with B.O.S. shop logistics. The process is still not capable of reaching low iron sulphur levels, less than 0.025%, reliably.

One of the factors which reduces soda ash efficiency is its high burn off rate as soon as it contacts the hot metal, material is lost to the atmosphere before it has time to react. This effect can be largely overcome by the use of soda ash in pellet form, and several proprietary combinations are available. Trials at the Normanby Park Works of the British Steel Corporation (ref.17.) have given good results with the pelletised material. However the problem of reaching low sulphur levels remains, and the pellets are considerably more expensive than the raw material.

Although the majority of works operating injection plants use calcium based desulphurants the method has been used with soda ash. In torpedo ladles the consumptions are high c.18kg/t to reduce iron of 0.03%S to 0.007%S, primarily because of the relatively shallow injection depths which are used. It can be inferred from Usinor results (ref.18.) that the slag causes severe refractory problems, particularly for the injection lance itself. These tests at Usinor in 200t. ladles produced the expected features of both soda ash and injection processes: heavy fuming, a limitation of injection rate because of splashing, a reduction in consumption for specific desulphurisation levels, improved reproducibility, and an ability to reach low sulphur levels. The deficiencies of the process are the long injection time, the very active slag which is produced, and a significant loss of silicon during the treatment.

The loss of silicon caused by the soda ash reaction is common to all soda ash treatments but data are scarce. At Usinor the loss was measured as 0.025%/kg soda ash/t.metal. This has a strong influence on the scrap/hot metal charge balance for the B.O.S. vessel and hence on the economics of the process. In an exercise at Appleby-Frodingham it was shown that the silicon loss negated the savings made by combining soda ash and carbide treatment in the transfer ladle to give a lower desulphurisation cost, (ref. 19.).

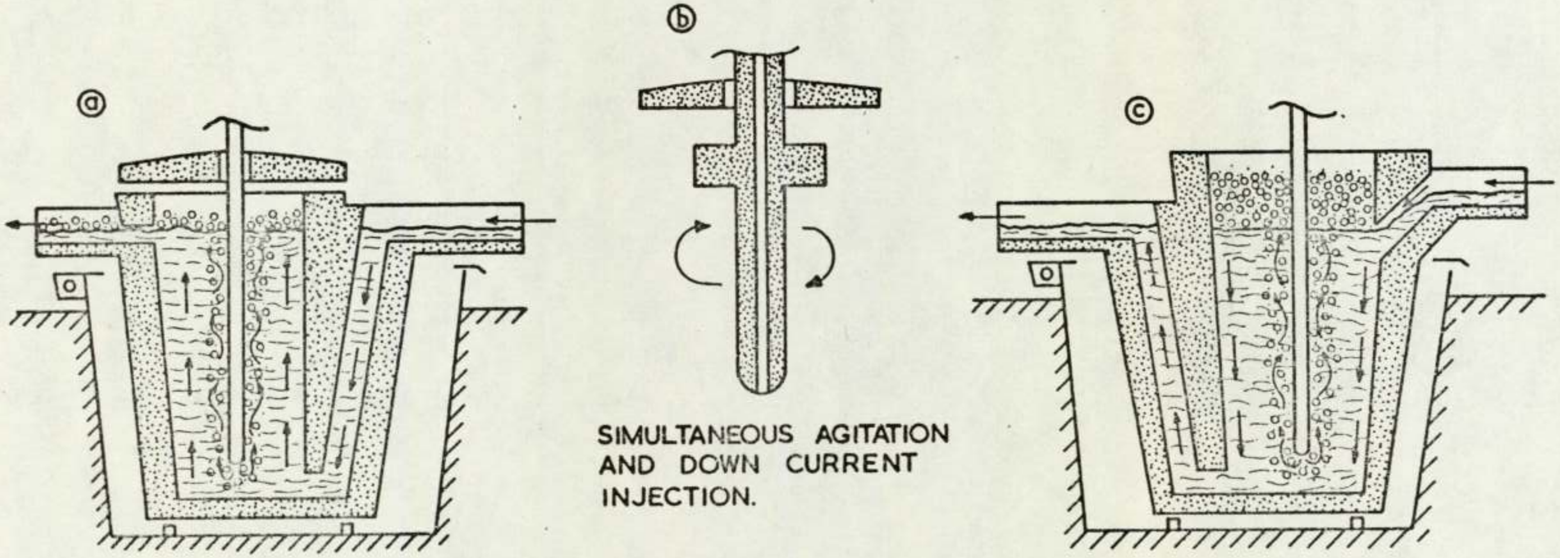
The combined problems of soda ash treatment prevent its use as a major desulphurising material.

2.3.3. Continuous Desulphurisation

Continuous desulphurisation is carried out by placing the desulphurising unit in the blast furnace runner between the slag trap and the hot metal ladle (ref. 15, 20-23). The process is still mainly operated on a small/pilot plant scale but has the advantage of limiting desulphurisation slag carry over to the steel plant without recourse to torpedo tapholes or separate ladle skimming units. Early work used the traditional materials: lime, soda, and lime-soda mixes, in tea-pot type ladles placed between the end of the runner and the metal transfer ladle. The process required some actual reladling and intermittent additions of the desulphuriser. Good efficiencies could be obtained but the method has been replaced by continuous and more controllable processes. Tests have been done with iron rates of up to 4t/min with the types of equipment in Fig.16 (ref.15). Calcium carbide was used as the desulphurant because of the rapid rate of reaction required.

It was found that the shape and capacity of the treatment ladle had a marked effect on the efficiency of desulphurisation. The residence time of the carbide i.e. lance depth, application rate, and iron flow rate being of prime importance. These criteria are opposed by the plant requirements of small vessels with low bath depths to reduce wastage. The same conditions except for lance depth apply if a mechanical stirrer is used with the carbide applied to the metal surface. The results of the trials are reproduced in Figs. 17 and 18, (ref.15). Percentage desulphurisation of 60 and 70 and 80% were obtained with additions of 5, 8 and 11 kg CaC_2/t. iron respectively. Unfortunately this equipment was built for injection only,

CONTINUOUS INJECTION EQUIPMENT



DOWN-CURRENT INJECTION.

SIMULTANEOUS AGITATION AND DOWN CURRENT INJECTION.

UP-CURRENT INJECTION.

FIG 16

UP-CURRENT VS. DOWN-CURRENT CONTINUOUS INJECTION

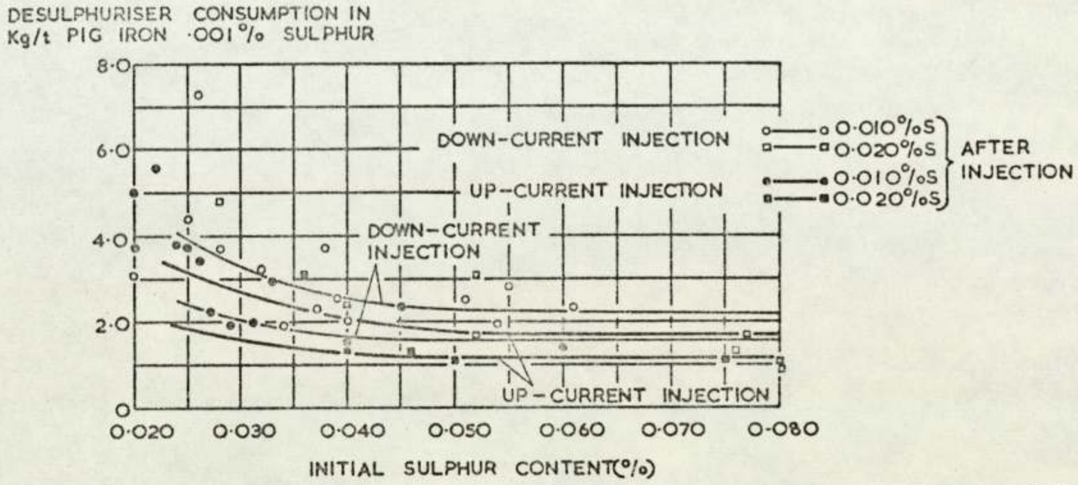
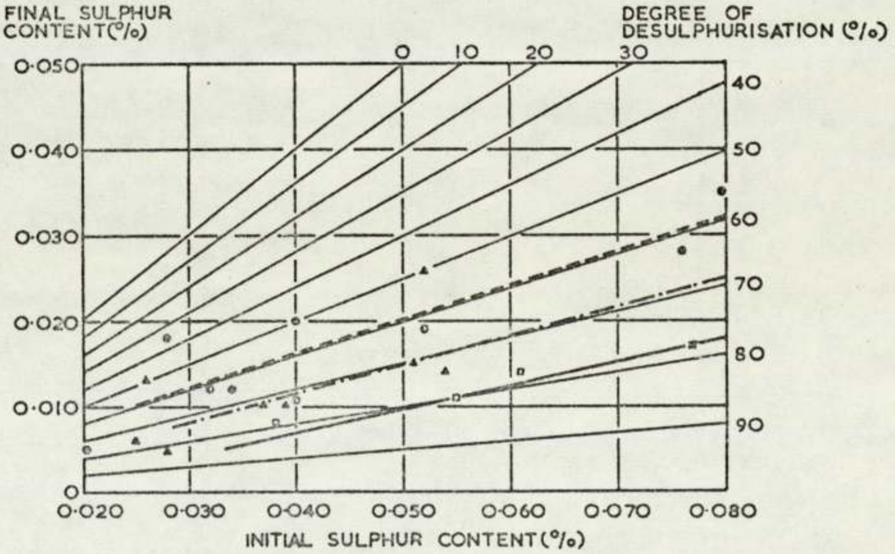


FIG 17

CONTINUOUS INJECTION AND STIRRING

EFFECT OF APPLICATION RATE



DESULPHURISATION PROCESS		CALCIUM CARBIDE APPLICATION RATE			CARRIER GAS			TAP RATE t/min	STIRRER SPEED r.p.m.
			Kg/t	Kg/min	TYPE	l/t	l/min		
CONTINUOUS DOWN CURRENT	INJECTION STIRRING + INJECTION	CALCIUM CARBIDE	o---o 5 ▲-·-▲ 8 □—□ 11	12 — 60	AIR NAT. GAS	70 – 1070	300 - 1500	○ △ □ 1·5 ● ▲ ■ 3·5 ● ▲ ■ 5·5	30 – 70

FIG 18

making the results for methods including stirring unsuitable for comparison with the pure injection data. The major conclusion of the work is that up current injection is more efficient than down current.

This is the expected result, and it appears from the points on Fig. 18 (ref.15), that the difference is significant at all initial sulphur levels. Little or no difference was found at the different tapping rates, it is possible that a cross over point between the two methods exists with respect to metal flow rate. Unfortunately no data is available to confirm this.

A nitrogen stir using a porous plug (Gazal) with calcium carbide addition to the surface has been used in America but only on a very small scale for foundry iron.

The largest continuous system in use is the Rheinstahl Quirl. A solid stirrer is rotated at about 70 r.p.m. in a metal pool 250 mm deep. At Henrichshütte it operates in the main runner of a 24 ft. dia. hearth blast furnace tapping 1500 tonnes per day at a maximum of 13.5 tonnes per minute. This system has been used with some success at B.S.C.'s Ravenscraig Works but is unsuited to the large tonnage that will need to be treated at that plant.

Desulphurisation tests in a standard covered top ladle have been carried out by the B.S.C. Corporate Laboratories in conjunction with an electro-magnetic elevator. The elevator is used to separate the product slag from the metal.

Units of this type are preferred to earlier attempts at continuous treatment involving more complicated systems, such as treatment in a rotary reactor, (ref. 24, 25).

The nature of the processes, taking iron directly from the furnace, means that the pre-treatment sulphur level cannot be accurately known. This, and the possible variations in casting rate make optimisation of the processes, with respect to final sulphur level and desulphurant consumption, difficult.

The problems of continuous treatment have resulted in batch desulphurisation being almost universally practised for large tonnage plants.

2.3.4. Desulphurisation with Ladle Stirring

Ladle desulphurisation techniques are generally applied where relatively small tonnages, normally 30 - 100 t. are to be treated and/or where very low sulphur levels are required.

The method employed is to dump the desulphurant on the surface of the metal which is then stirred to give intimate mixing between the two.

The most common stirrers are of the paddle type, hollow as the Demag-Ostberg Fig. 19 (ref. 14), and solid on the Rheinstahl Fig. 20 (ref. 14, 27), and K.R. (Nippon Kokan) Fig.21 (ref. 26) designs. The German devices are only partially immersed in the metal and it is claimed that this is particularly advantageous with respect to efficiency.

The hollow stirrer is rotated at 80 - 90 r.p.m. A centrifugal force is set up in the inclined hollow arms which draws metal through the vertical pipe. This system should be better than the solid Rheinstahl stirrer rotated at about 70 r.p.m. since even with an optimum choice of paddle length to ladle diameter, the potential mixing of the hollow stirrer should be greater. In practice there is little difference between the two methods and the solid stirrer tends to be favoured because of the reduced wear and maintenance problems.

The effect of the degree of mixing on overall efficiency has been shown with tests using a solid stirrer Fig. 22. The stirrer length and speed should be the maximum possible allowing for spillage from the ladle, stresses on the ladle lining, and the build up of skulls around the ladle. It was also found that at high rotating speeds the stirrer became rotationally symmetrical through deposits and slag formation. The metal weights treated in this fashion as reported vary from 40 - 95 t.

HOLLOW STIRRER FOR DESULPHURISING LIQUID IRON DEMAG-ÖSTBERG TYPE

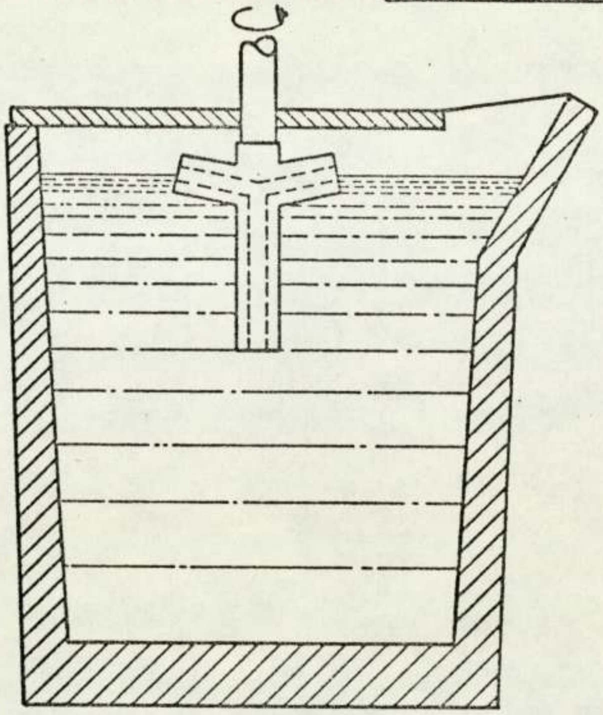


FIG 19

SOLID STIRRER FOR DESULPHURISING LIQUID IRON RHEINSTAHL TYPE

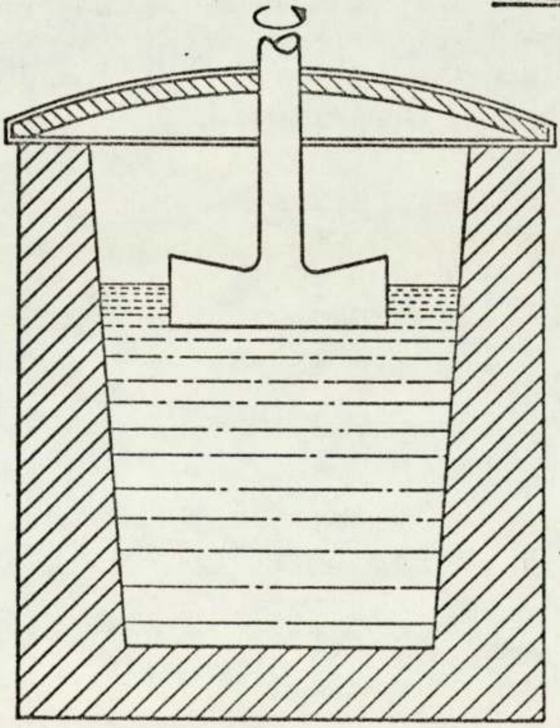


FIG 20

K.R. STIRRER FOR DESULPHURISING LIQUID IRON

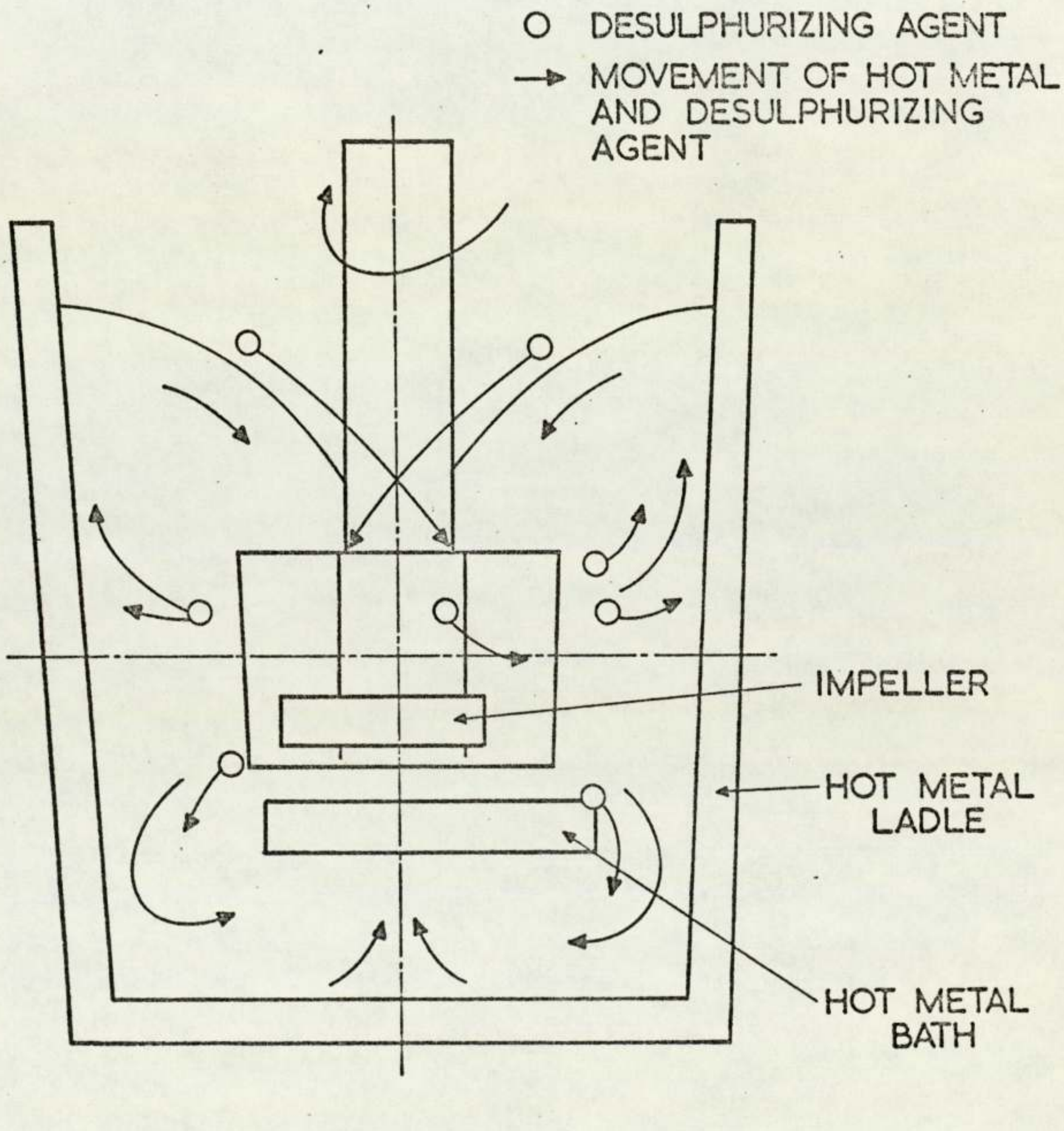


FIG 21

EFFECT OF AGITATOR ARM LENGTH AND ROTATIONAL SPEED

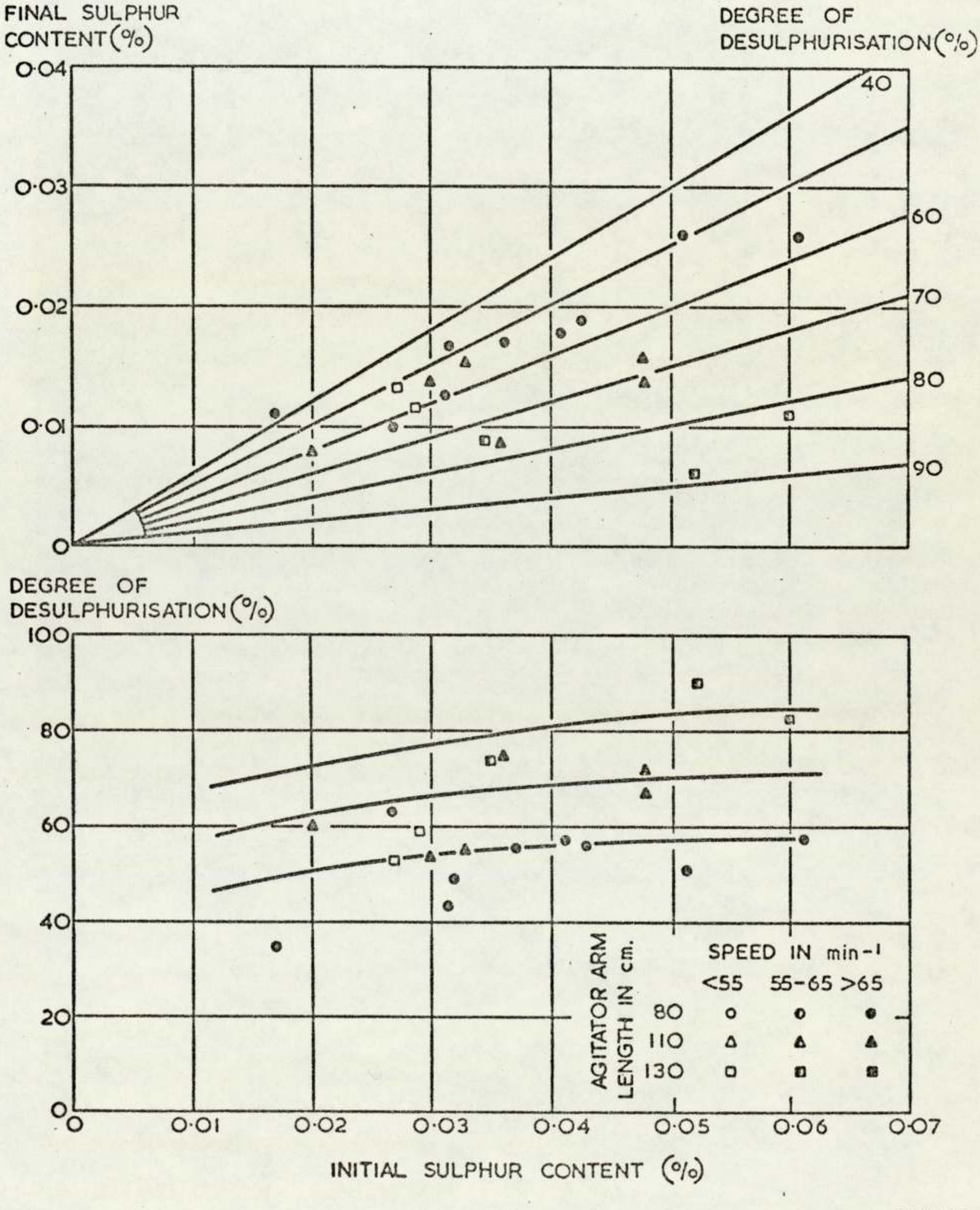


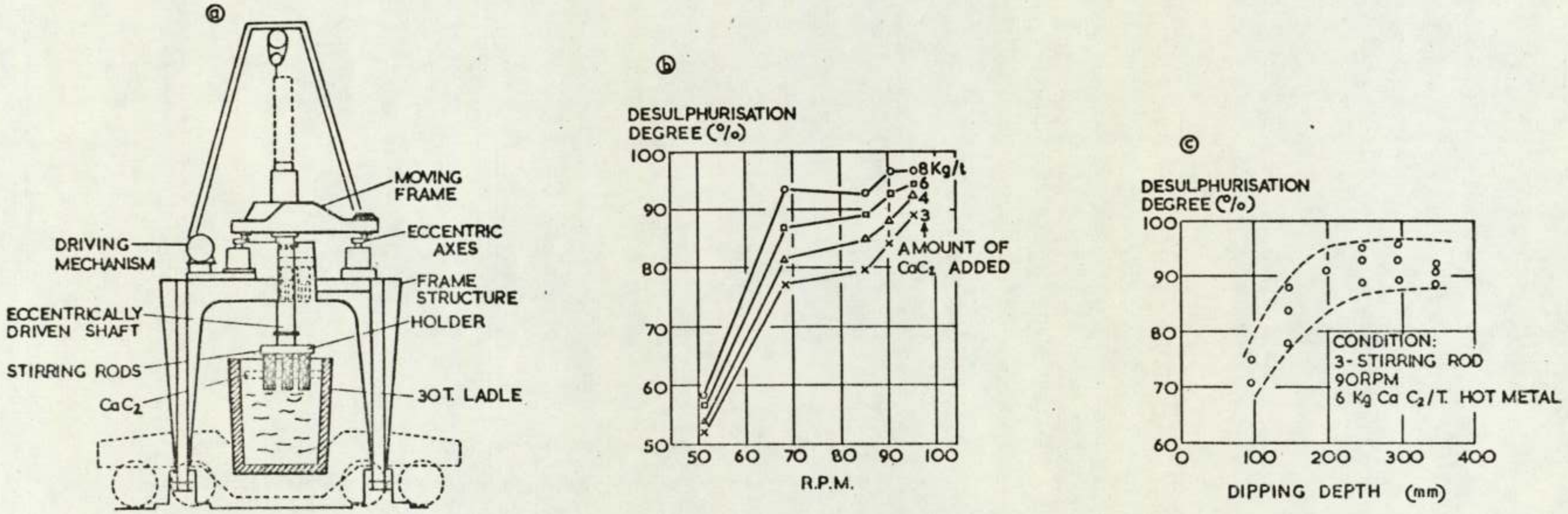
FIG 22

The K.R. process was developed to produce very low sulphur hot metal treating 30 - 40,000 t. per month in 120 - 160 t. batches. The impeller 1,300 mm o.d. and 720 mm high is rotated at an immersion depth of 1200 - 1400 mm at 70 - 120 r.p.m. The eddy current depression gathers the reagent which is redispersed by the impeller action, Fig. 21, (ref. 26). Calcium carbide 70 - 80% pure is used as the desulphurant. The results from this process contradict the German claim for partial immersion of the stirrer giving better mixing efficiencies. The probable explanation lies in the different metal weights and ladle depths. It would seem that the surface stirrer does not produce enough mixing energy to sufficiently agitate the larger mass of metal. The K.R. process is now used on units of up to 300 t.

The problem of mixing could be overcome by the use of an immersed lance for stirring only or by bubbling gas through using a porous plug (ref. 28, 29) as in the CTIF - Volianik, (ref. 30), and Gazal (ref. 17, 31, 32) processes. For larger metal weights however the material injection processes are more suitable.

Other units used to induce ladle mixing, include eccentric based stirrers and shaking ladles. A pilot scale unit using the former technique was used by Nippon Kokan in 30 t. ladles, (ref. 33) Figs. 23(a) and (b) showing the general arrangement and results obtained. This process seems to have been superseded by the simpler K.R. process, but the results on immersion depth Fig. 23(c) show the weakness of surface stirrers if not operating under optimum conditions of relative size and metal depth.

ECCENTRIC STIRRING FOR DESULPHURISATION



STIRRING SYSTEM.

EFFECT OF ROTATIONAL SPEED ON EFFICIENCY.

EFFECT OF IMMERSION DEPTH OF RODS ON DESULPHURISATION EFFICIENCY.

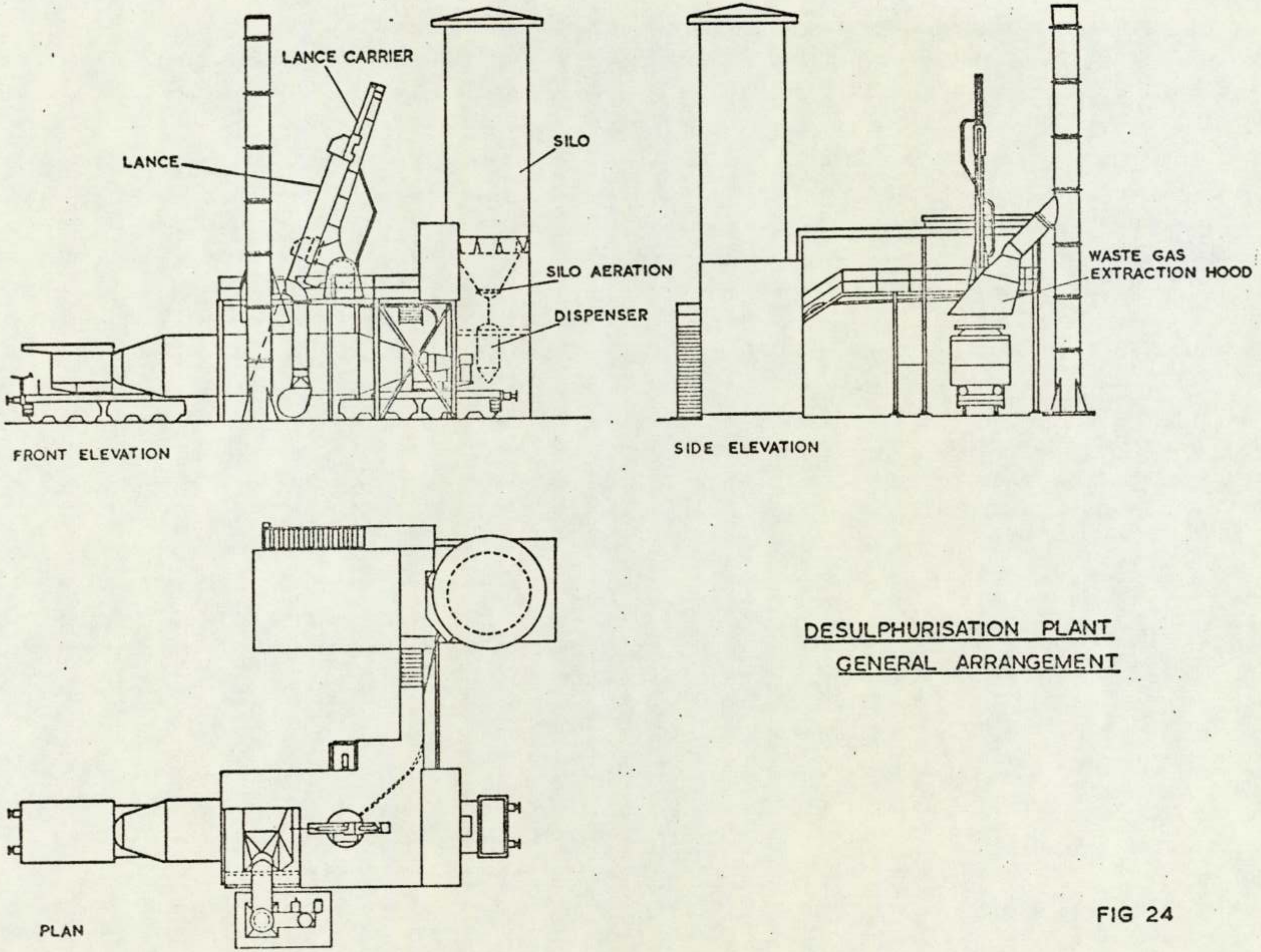
FIG 23

Shaking ladles, (refs. 9, 34-37), were first used in 1959 but have been slow in application for larger steel processing units and foundries because of the engineering difficulties involved.

The method makes use of the increase of surface area made available by the eccentric revolution, and the stirring action caused by the metal breaking like a wave around its periphery. A variant of the basic method is the D.M. convertor, (ref. 38-40), in which the direction of revolution is alternated. Several shaking ladles are in use of 30 - 60 t. capacity and one Swedish plant until recently had a 100 t. unit.

2.3.5. Desulphurisation by Injection

The technique of agent injection is used for both the standard hot metal and torpedo ladles. Torpedo lades are widely used throughout the world for the transport and short term storage of iron between the ironworks and the steel plant. The planning of a desulphurisation operation is complex; suffice it here to say that in a modern fast production steel plant re-ladling processes cannot be tolerated and unless other within-shop facilities can be accommodated, desulphurisation in torpedo lades is necessary, and has its own particular problems. A general arrangement of a torpedo injection station is shown in Fig. 24. Of necessity there is little variation in the construction and layout of an injection plant. The system used at Appleby-Frodingham Works will be outlined here and may be taken as typical.



DESULPHURISATION PLANT
GENERAL ARRANGEMENT

FIG 24

The desulphurising mix is delivered to the plant by road tanker and unloaded into the main storage silo, capacity 70 t. Nitrogen is used as the carrier gas for transport of the material. The silo empties into a dispenser of 2 t. capacity, sufficient for a single treatment in the normal working range of sulphur contents. The agent is pumped from the dispenser into the metal via a refractory coated lance. This is most commonly a mild steel pipe 1 - 1½" internal diameter with a high alumina cement coating.

The basic layout and operation of a transfer ladle plant is the same as that described for the torpedo system.

At Appleby-Frodingham Works the two substances making up the agent are mixed before delivery to the plant. Other units, using less compatible materials with respect to pneumatic transport, have separate storage and dispensing facilities for the primary and secondary agents. Nitrogen is used as the delivery gas, air (dried in the case of calcium carbide) is also used.

With an injection technique the time available for reaction is that which the desulphuriser takes to rise to the surface of the metal, since there is only limited remixing of the slag that is formed. Four factors are therefore of prime importance: the immersion depth of the lance, the material delivery rate, the rate of mixing of the metal, and the reactivity of the desulphuriser. The first is easily controlled and can be optimised for any particular plant conditions.

Several methods are used to obtain a high degree of mixing. The easiest are to increase the carrier gas/gas evolving agent flow rates but problems can occur due to excessive splashing and particle retention by the gas bubbles. Multinozzle or multi-lance practices are used. Their effectiveness depends on their configuration and the shape of the treatment vessel.

For example, not much is gained by using more than a single injection lance in a cylindrical metal ladle. Metal flow patterns in torpedoes have been investigated and will be discussed later.

The method to increase mixing used at Appleby-Frodingham is to inject a compound which will decompose at the metal temperature, calcium carbonate is used and this is the most popular material in use in the world today. A highly reactive desulphuriser is required, calcium carbide and calcium cyanamide being commonly used, the former at Appleby-Frodingham. The efficiency of reaction is increased by the presence of a reducing agent either injected with the mix as a solid or in the form of a gas to give reducing conditions in the reaction zone. The Appleby-Frodingham reagent has carbon present for this purpose. Some plants use lime or lime/soda injection and almost invariably use a hydro-carbon gas as a reaction aid.

Using the hydro-carbon gas enables reasonable efficiencies to be obtained at relatively low cost. The great handicap of lime as a desulphurant is the relatively large specific consumption, measured in kg/t. iron/0.01%S removed, required. This means that larger slag volumes have to be removed from the metal, and greater freeboard left above the metal before treatment, thus reducing the plant throughput considerably.

2.3.6. The Use of Magnesium for Desulphurisation

The discussion so far has concentrated on calcium based reagents, since these are the most commonly used. However a number of plants do use magnesium as the basic reagent.

Magnesium is a powerful desulphurant, both because of its chemical affinity for sulphur and because the desulphurisation reaction is between a gas and a liquid rather than a solid/liquid as for calcium compounds. The major problem with magnesium is controlling the vigour of its reaction, the large gas volume produced as it reacts can cause excessive and dangerous metal splashing. Several processes have been developed for its use in both open and torpedo ladles. Even though magnesium consumptions are low compared with calcium carbide treatments it is generally a more expensive process. (Magnesium cost in the U.K. is c.£1300/t. but varies widely around the world and this is reflected in the degree to which it is used in particular countries.) However its high efficiency does promote its use where very low sulphur levels are required because of the low slag bulks produced and the relatively short treatment times.

2.3.6.1. Magnesium Immersion, 'Dunking', Process

Before the general expansion in the use of injection techniques the most common process was to plunge coke, impregnated with approximately 45% Mg, into the iron. This material is normally referred to by its trade names of Mag-coke or Galag. The small pore size of the coke ensures a gradual release of magnesium into the iron. Typical apparatus for the process is shown in Fig. 25. It consists of a bell normally of concrete or graphitised refractory in which a drum of the Galag is held. The holes in the bell allow the vaporized magnesium to jet into the surrounding metal. The bell is normally suspended from a counterweight, which also serves as a beam for resting on the ladle or torpedo mouth during the treatment.

Variations of this idea with alternatives to coke have included magnesium impregnated compressed steel shavings, magnesium-dolomite, and refractory/insulating material composits (refs. 41,42.). In all cases the magnesium consumption for a given sulphur removal tended to be higher and the violence of the reaction greater.

SCHEMATIC OF GALAG PLUNGING SYSTEM

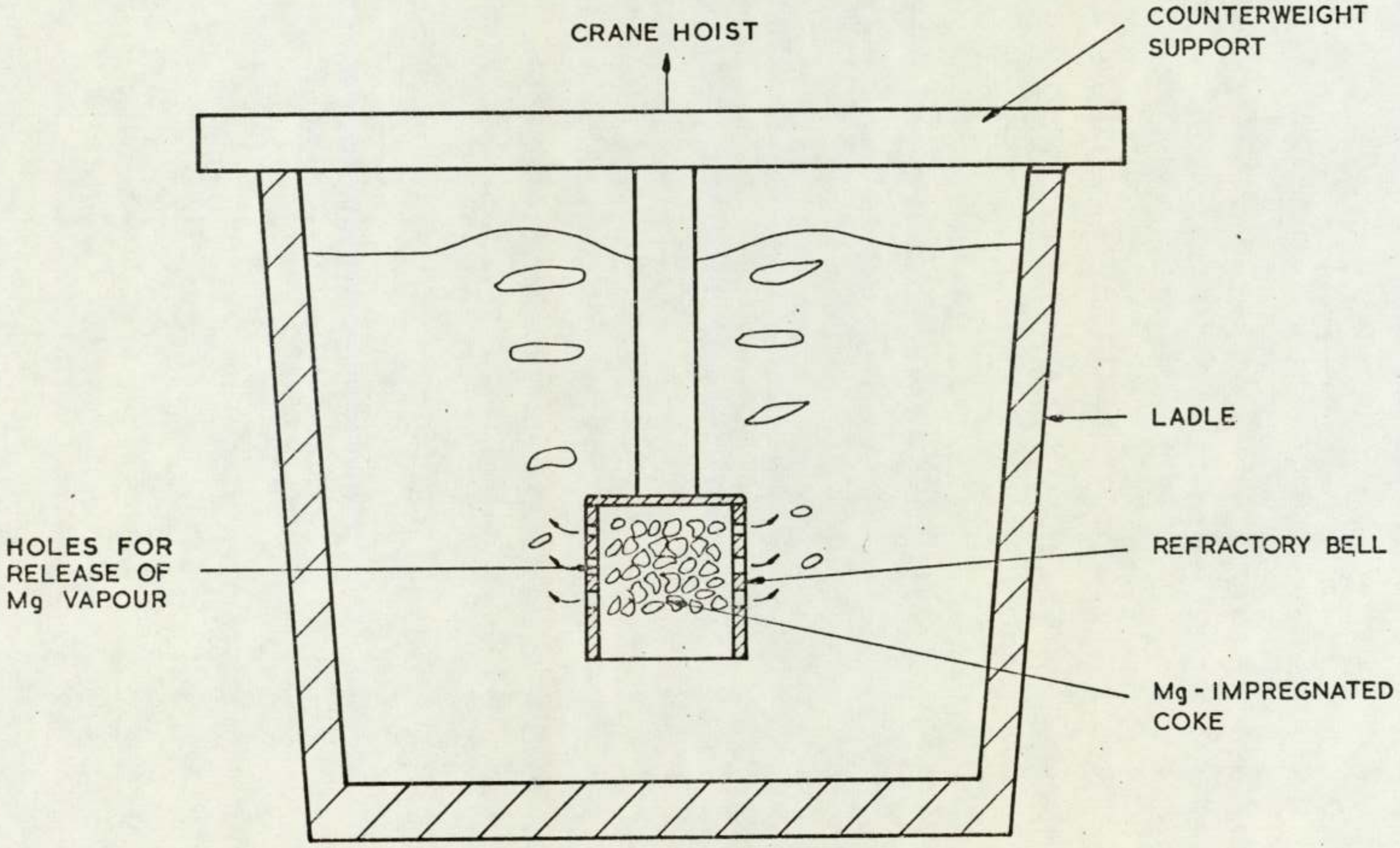


FIG. 25

The dunking process finds its principal application in open transfer ladles and as such has been tested at some time at the majority of steel plants. Typical results are shown in Fig. 26. Although reproducibility of results is quite good its principal disadvantage (excluding cost consideration) is that the weight of magnesium added is fixed. Therefore for steel plants where the iron sulphur content is variable and/or high either multiple bell or multiple treatments per ladle are required with only a limited amount of control over the final sulphur level. Where the iron supply is more consistent the efficiency of the process can be increased considerably by gas stirring of the iron during the treatment, (refs. 43, 44) Fig. 27. This modification known as the H - S process has an additional advantage in that the stirring gas is used as an aid to removal of the post treatment slag. This technique and its benefits are discussed later.

A number of plants have used the dunking method in torpedo ladles. This causes no problems as long as the torpedo length to diameter ratio ($^{l}/d$) is sufficiently small. In torpedo trials at the Scunthorpe Works of B.S.C., with a torpedo $^{l}/d = 6$, the immersion depth of the bell was too small to produce good metal mixing from the magnesium vapour evolved, and poor desulphurisation results were obtained.

HOT METAL DESULPHURISATION RESULTS USING GALAG

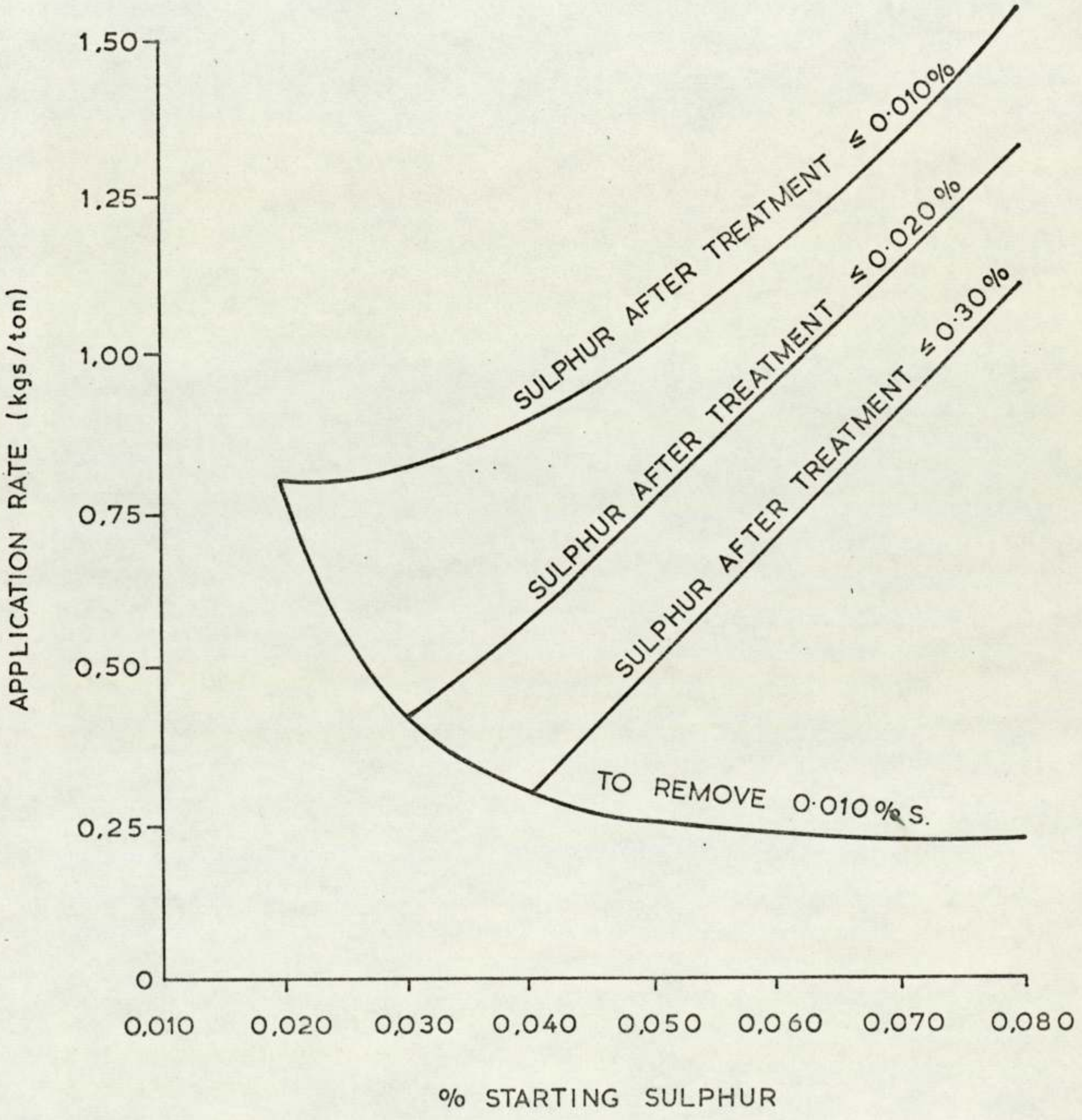


FIG. 26

EFFECT OF GAS STIRRING ON THE GALAG DUNKING PROCESS

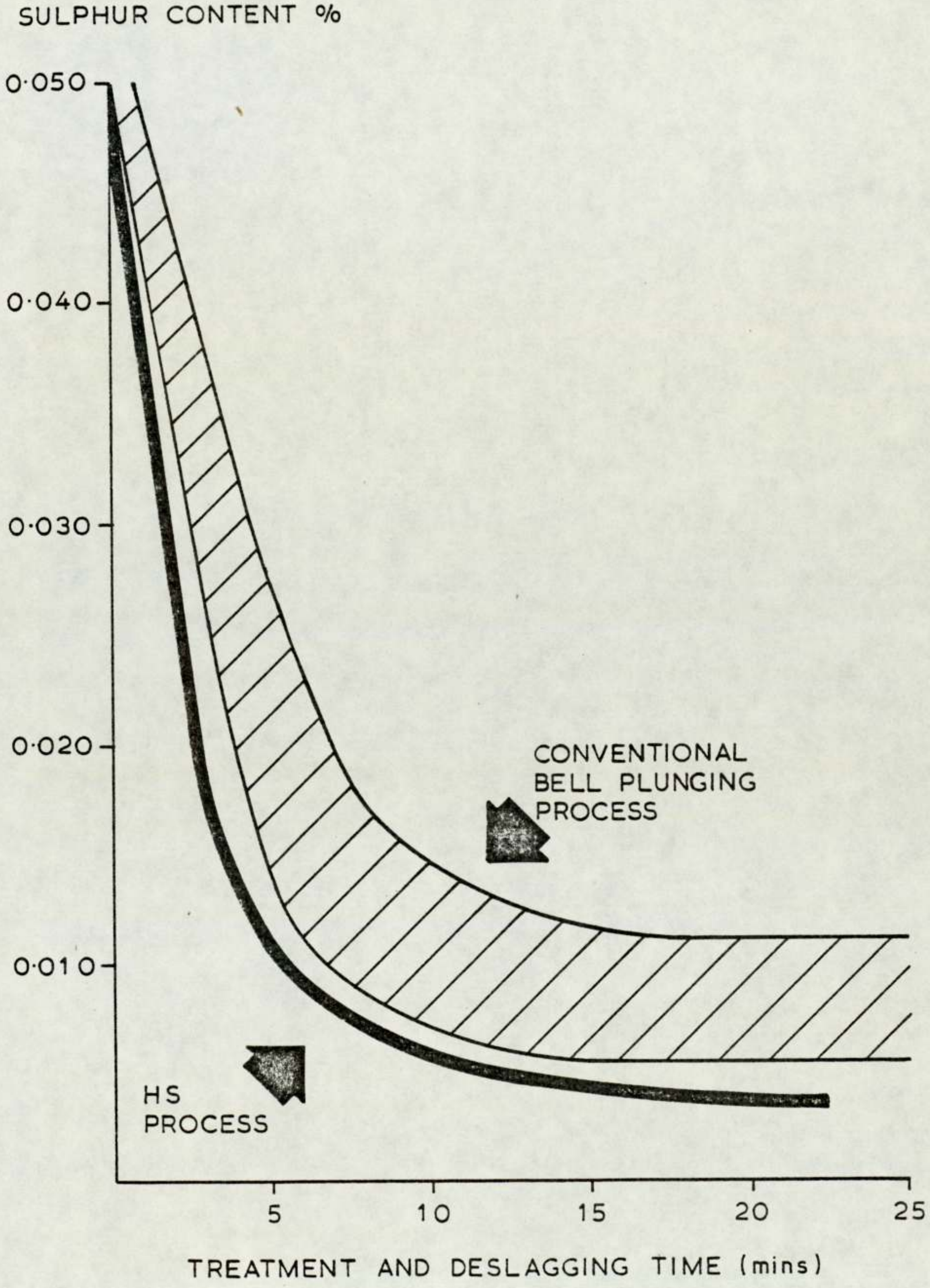


FIG. 27

2.3.6.2. Magnesium Injection

Magnesium is successfully injected at several plants. The difficulty with the process is that the magnesium must be introduced at a very low rate which must be closely controlled.

The injection of pure magnesium granules is reported as being practised in the Soviet Union but little detailed data is available. It is a hazardous process and it is usual for the magnesium to be mixed with a carrier material. This is normally alumina, lime or both.

Experience with Mg/Al_2O_3 injection into 300 t. transfer ladles showed that a magnesium rate of 15 kg/min, as a 50/50 mixture was excessive, (refs. 45, 46) the turbulence produced becoming acceptable at 8 kg/min. The efficiency of the process increases as the injection rate is reduced, this again is the conflict between agitation energy and the time for chemical reaction. As for all magnesium based desulphurisation the efficiency increases with decreasing metal temperature. Reversion of sulphur from magnesia slags should not be a problem. It has also been shown that the desulphurisation is improved by the formation of a basic cover slag on the hot metal, by the addition of lime. Without the cover slag it was also found that low sulphur contents, i.e. less than 0.005%, could not be reached reliably.

A possible explanation of this effect is that the magnesium reaction product is in very fine particulate form and because of the turbulence some of this remains entrained in the metal and therefore appears within a total sulphur analysis. Although some reaction will take place with a highly basic slag in a turbulent system it is more likely that the slag acts as a retainer for the MgS formed. A claim of the H - S process is that the gas stirring (much less violent than magnesium vapour evolution) helps the flotation of MgS from the metal. Typical results for the Mg/Al_2O_3 process are shown in Fig. 28.

Although the alumina mixtures are successful a more common solution at the moment is to mix the magnesium with lime, the Lime-Mag process as developed by Jones and Laughlin. The method gives good reproducible results. It has the advantage of adding the lime for the slag with the magnesium and is therefore easier to operate. However there are two significant drawbacks:-

1) Magnesium and lime are non-compatible materials with respect to pneumatic transport. It is therefore preferable to use separate dispensers and blend them at or close to the injection lance.

2) One of the advantages of magnesium is the low slag bulk produced, both with respect to its removal from transfer ladles and the dangers of build up in torpedo ladles.

MAGNESIUM INJECTION INTO TRANSFER LADLES — RESULTS

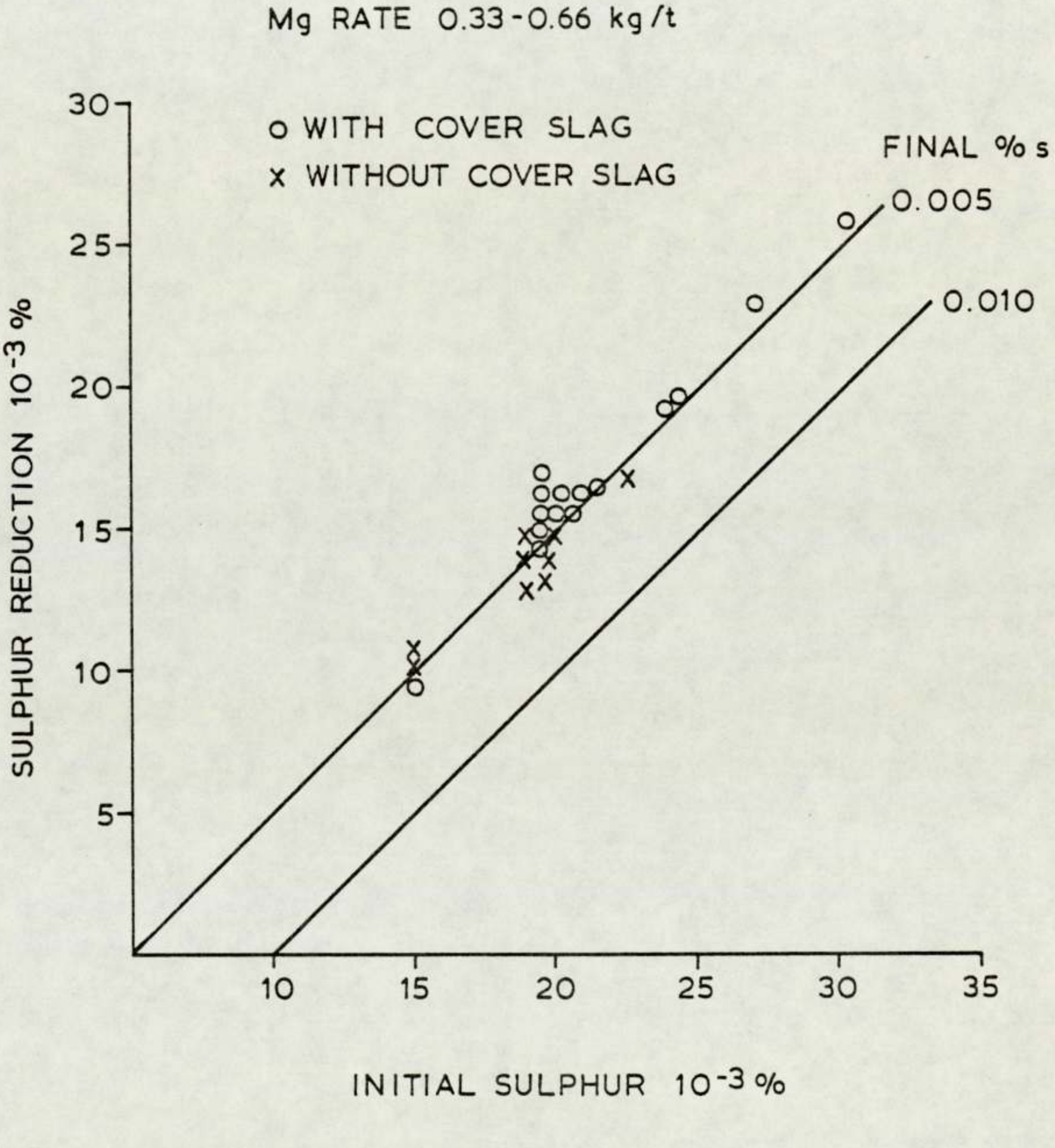


FIG. 28

The use of lime as a diluent removes this advantage.

A recent development which has the advantages of magnesium without the disadvantages of a carrier material is the use of pelletised magnesium or salt (NaCl, KCl,MgCl etc) or oxide (MgO) coated magnesium granules. In each case the treatment process reduces the rate of gas evolution. Reported results (refs. 47, 48,) show 5-15% higher magnesium utilisation (dependent upon intial sulphur level) than the alternative processes. However the pelletised product, in particular, is expensive relative to other forms of magnesium.

2.3.7. Further Process Details and Results of Desulphurisation Processes.

A great variety of operating conditions are possible for the same materials used in the same type of process. These can yield many different significant operating results. In this section the following are considered:

1. Material
2. Material size
3. Process Vessel shape
4. Quantity of metal
5. Method of application
6. Method of agitation

Tables 4 and 5 summarise the significant combinations of these variables and give a guide to the general operating and desulphurising efficiencies to be expected.

TABLE 4

Material Size Gradings Used (where available)

Classified by Process

(Material Code–Table 2)

Process 1. Injection

Material	1.						
Size mm	Wt. Percentages in each Size Range						
+ 1.7							
1.4			2.2		.7		
1.0			33.8	13.4	11.8		
.9							
.8			38	38	24.4		.3
.7							
.6		< 1%	20.8	41	23.3	.4	8.0
.5	95%						
.4			3.2	4.7	22.8	27.2	19.4
.3		9%					
.2			.7	.9	6.1	24.2	19.6
						.15 -27.3	24.9
.1			.4	.7	5.2	.106-15.1	13.7
.09			.9	1.0	5.7	5.8	14.1
.08 .07		20%					
.06							
.05							
.04		70%					
.03							
.02							
.01							
Size Code	A	H	I	J	K	L	M
Iron Wt.	30-40t	80t			0.4 - .5 t		
Treated and Temp °C	1320-1350				1500°C base		

TABLE 4 (Cont'd)

Process 1. Injection (Cont'd)

Material	2		3		4		5		6	11
Size mm	Wt. Percentages in Each Size Range									
+ 1.7										
1.4										0.1%
1.0										
.9										
.8										
.7										
.6										
.5										
.4					98%					
.3						2%		2%		39.9%
.2					Na_2CO_3		2%			
.1										
.09			42%						25%	
.08			57%			22%		22%		
.07							23%			
.06	100%		$CaCN_2$						75%	60%
.05										
.04										
.03						76%		76%		
.02	CaC_2						75%			
.01		99%		99%						
		$CaCO_3$		$CaCO_3$		CaO				
Reference Report	1		1			5	1	5		13
Size Code	B	C	D	C	E	F	G	F	A.F. Plant	R
Mix Ratio	85/15		70/30		99% Na_2CO_3		100%	CaO	75% CaC_2 25% $CaCO_3$	70% $CaCN_2$ 30% Diamide Lime
Iron Weight	27-42 40-60 130-1360		25-32/50-200 75-206/75-102		80		20-45	80	150-250 t	200-450 t
Temp.	1300/1580		1250-1320				1260-70			

TABLE 4 (Cont'd)

Process 2. Stirring

Solid Stirrers

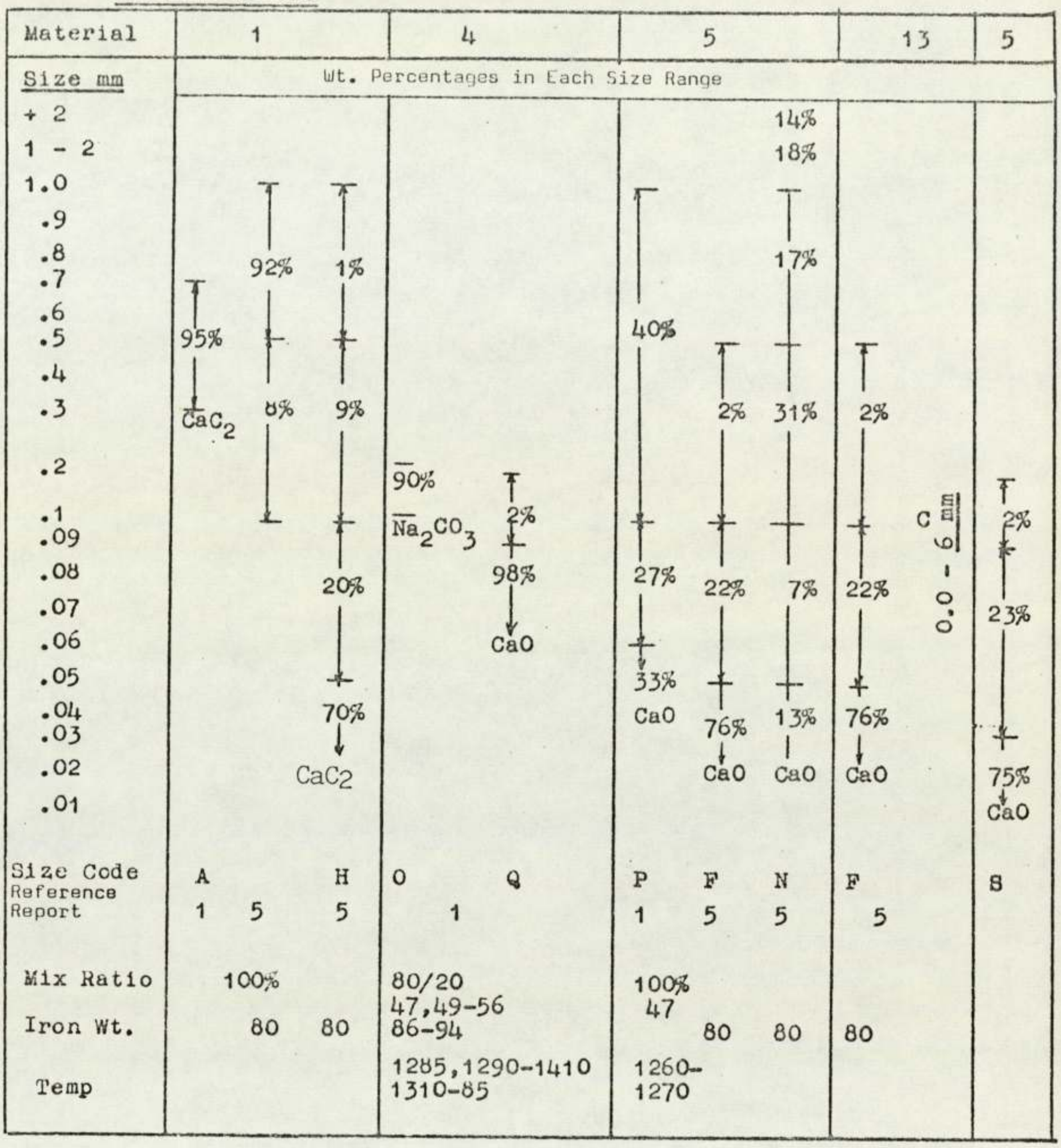


TABLE 4 (contd.)

Process 2. Stirring

Hollow Stirrers

Material	1	4	
Size mm	Wt. Percentages in Each Size Range		
+ 2			
1.2			
1.0			
.9			
.8			
.7			
.6		40%	
.5	95%		
.4			
.3			
.2	CaC_2		
.1			90%
.09			Na_2CO_3
.08		27%	
.07			
.06			
.05			
.04		33%	
.03		CaO	
.02			
.01			
Reference	A	P	O
Report	1	1	
Mix Ratio	100%	10/1 9/1	7/3
Iron Wt. t	62-95	8.5-16 66-78	
Temp °C	1250-1370	1230-1330	

TABLE 5

Relative Efficiencies of Desulphurisation Processes

(Material Code - Table 2, Size Code - Table 4)

Method	Material	Size	%DS	Tonnage	Kg/t.iron Consumption	T°C
Injection	1	A	64*	30-40	3	1320-
			73*		4	1350
			82*		6	
			87*		8	
			(62-100*			
		H	(55-65	70	3.5	@ 25 Kg/min
			(80-100*			
			(72-80		5.0	
			(100*			
			(97-88		6.5	
			50-66		3.5	@ 35 Kg/min
			65-73		5.0	
			69-85		6.5	
			(80*		3	1300
			(84*		4	1360
	2	B/C 85/15	(100*	27-42	5	1300
			100*	40-60	9.5	1380
	3	D/C 70/30	45*	Foundry Pig Iron 50-200	4	
			70*		8	1250-1320
			80*		14	
			63*	25-32	4	
			75*		8	
			75*	75-206	10	
			81*		14	
				Foundry Pig Iron		
			85*	75-172	4	
			83*		8	
			95*		14	
	4	E/F 99% Soda	(100*-84*			
			(73-74	70	12	@ 40 Kg/min
			(80*-73*			
			(58-64		12	@ 80 Kg/min
	5	F	(67*-48*	70	7	@ 40 Kg/min
			(50-42			
			(100*-76*			
			(73-67		12	
					16	
					7	@ 80 Kg/min
					12	
					16	

TABLE 5 (contd.)

Method	Matl.	Size	% DS	Tonnage	Consumption	T °C
Stirring	1	A	100*	85-95	≫ 4	1360- 1280
			78*		4	1345-
Solid Stirrer			100*	42-50	≫ 6	1415
		A	100*	45-47	8	1260- 1310
			(100*			
		H	(80-90	75	5	
			(67	0.5	8.4	
		I-M	(No appreciable diff. in size grading vs % DS			
	4	O/P 1/9	82*	86-94	(6	1345- 1375
			100*		(10	"
			85*		(7	
			90*		(10	1340-
		O/Q 2/8	100*	86-94	(13	1385
			70*		(5	1290-
			90*	49-56	(7½	1410
			92*		(5½	
			100*		(10	1285-
			100*	47-48	(13	1290
	5	Q	57*	47-48	(7½	1260-
		S	60*	20-45	(10	1270
	5	F	80	75	10	
		F+Carbon	35	75	10	
			96*	62-95	(4	1250-
Hollow Stirrer	1	A	100*		(6	1350
			96*		(6	1275-
			100*	77-95	(8½	1370
	4	P/O 10/11	65*	85-16 Cupola	7	1230-1330
			90*		10	
			98*		15	
			98*		(8	
		9/1	95*	67-78 Thomas	(12	
			65*	Thomas	(7	
		7/3	80*	66-69	(9	

TABLE 5 (Continued)

Method	Material	Size	%DS	%S in.	Tonnage	Kg/t. iron consumption	T°C
Injection	11	R 70/30	89	023	200	13.2	@ 80-100 Kg/min
			93	038		18.8	
			95	055		25.1	

TABLE 5 (contd.)

Stirred by Injection

Material 1 on surface

Optimum size 5.08 - 10.16 mm granules
dust free

Tonnage ~10-12 t.

The best reaction efficiencies, measured either by percentage desulphurisation or percentage calcium utilisation at low reagent consumptions are obtained by those processes which optimise desulphurant reactivity and the creation of conditions where sulphur is brought into contact with the reagent.

The operating results of the various processes follow.

2.3.7.1. Ladle Stirring Processes (refs. 13-15, 26)

Lime is the least powerful reagent used, it being difficult to obtain over 70% desulphurisation from high initial sulphur levels even at high reagent consumptions (kg/t). This makes the efficiency particularly dependent on particle size and mixing efficiency, the coarser grades quoted give up to 20% less efficient desulphurisation, than the finer blends.

It is far more common therefore for lime to be mixed with soda ash. This produces a marked improvement in performance which increases with the proportion of soda in the mix. Although the lime is of decreased importance in the process, the effect of a reduction in its particle size is still significant. The use of soda not only provides a secondary source of desulphurisation but produces a considerably thinner slag than a pure lime process. This is beneficial in two ways. Primarily, the more fluid slag is more easily mixed with the metal during the process, and secondly the final slag can be easier to remove if used with the correct proportion of lime. It should be noted however that soda slags are notorious for their vigorous attack of ladle refractories. Because the soda decomposes at or near the surface of the iron the gas produced will not significantly increase the stirring of the metal.

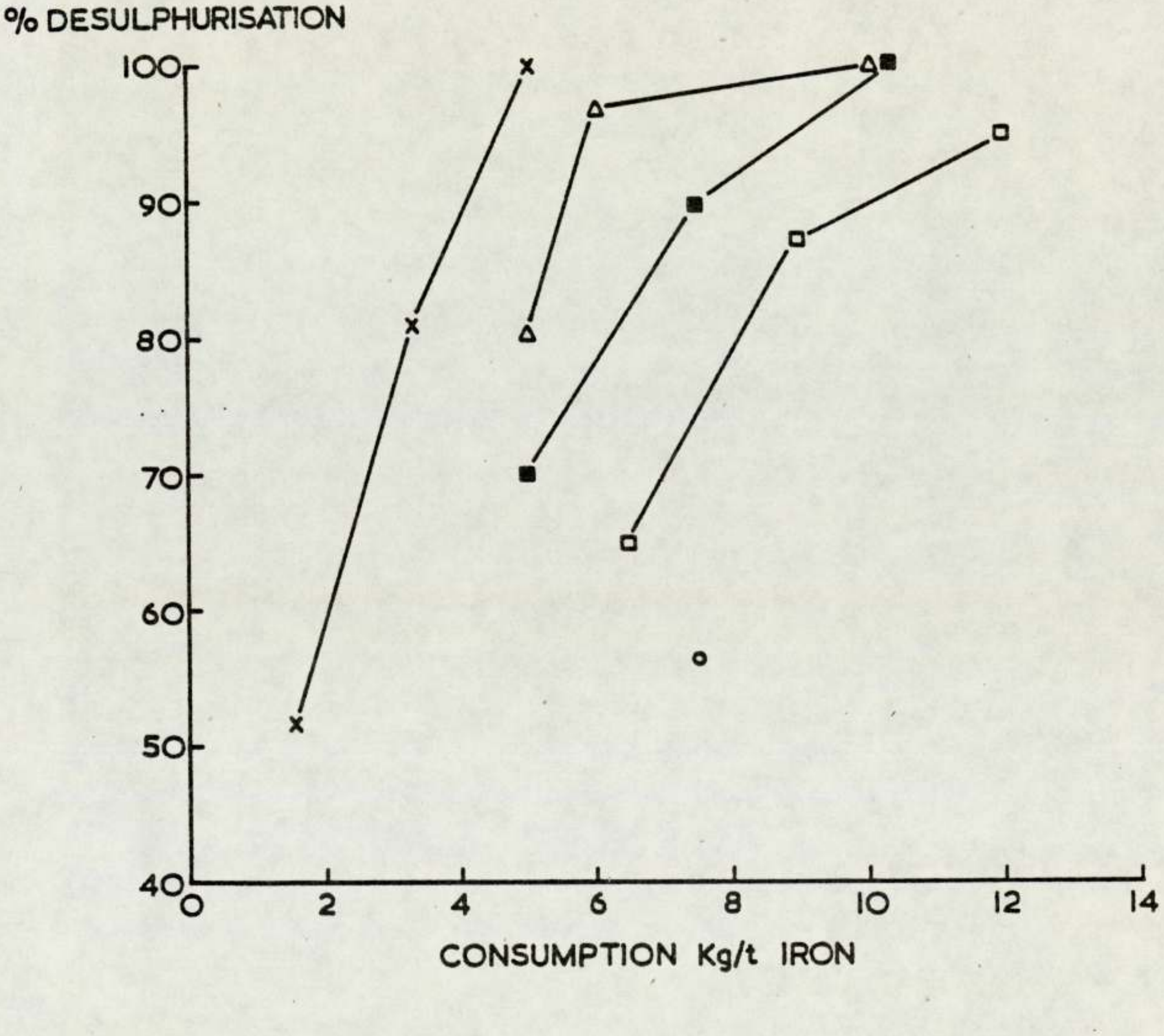
The action of lime is also enhanced by providing a reducing atmosphere over the stirred ladle.

The best results for stirring processes in terms of performance (normally economics) are obtained with calcium carbide as the desulphurant. Fig. 29 compares the desulphurising efficiency obtained by the various stirring processes. It should be noted that CaC_2 gives a reducing atmosphere over the metal.

2.3.7.2. Injection Processes

The reasons against using lime for a stirring process are even more applicable when considering desulphurisation by injection (refs. 13-15, 49-52). During the injection process the desulphurant is only effectively mixed once with the metal, high reagent reactivity is therefore extremely important. Desulphurisation as was practised at Clyde Ironworks (B.S.C.) using lime and nitrogen plus propane as the carrier gas is probably the nearest to a pure lime process that is economically feasible. The injection was into open top ladles and required about 14 kg lime/t. of iron for an 0.04% to 0.02% sulphur drop. This consumption of reagent would be much too high to use in torpedo ladles because of the slag volume produced.

DESULPHURISATION USING MECHANICAL STIRRING RELATIVE EFFICIENCIES



	HOLLOW STIRRER (DEMAG-OSTBERG)	SOLID STIRRER (RHEINSTAHL)	SOLID STIRRER K.R.–N.S.C.
LIME	○		
LIME/SODA	□	■	
CaC_2	△	▲	x

FIG 29

Increased desulphurisation is achieved by using calcium cyanamide, (refs. 13, 14, 53). Lower consumptions are required than with lime Fig. 30. Desulphurisation by injection using calcium carbide as a base is the most popular process in use today, (refs. 13-15, 54-62). Calcium carbide is suitable for open top cylindrical ladles where good efficiencies are obtained. In torpedo ladles however, efficiency is reduced because the metal is not sufficiently agitated by normal amounts of carrier gas to bring the sulphur to the reaction zone.

This is overcome by the addition of calcium carbonate. Fig. 31 gives results obtained at Appleby-Frodingham torpedo treatment plant with this process. If the process is operating under ideal plant conditions the material consumption should be 0.9 to 1.1 kg/t./0.01% sulphur removed.

In the open top cylindrical transfer ladle, carbide efficiency can be improved by the use of a carbonate addition but a much lower content is required. The transfer ladle plant gives similar desulphurisation performance to the torpedo unit. However because the system has inherently better mixing characteristics and because of the practical problems of torpedo operation (as will be discussed later) the variability of results is significantly reduced.

Previous work has shown that efficiency of desulphurisation is dependent on the reagent, the initial sulphur level of the iron, and the metal mixing ability of the process.

INJECTION INTO OPEN TOP LADDLE RELATIVE EFFICIENCIES

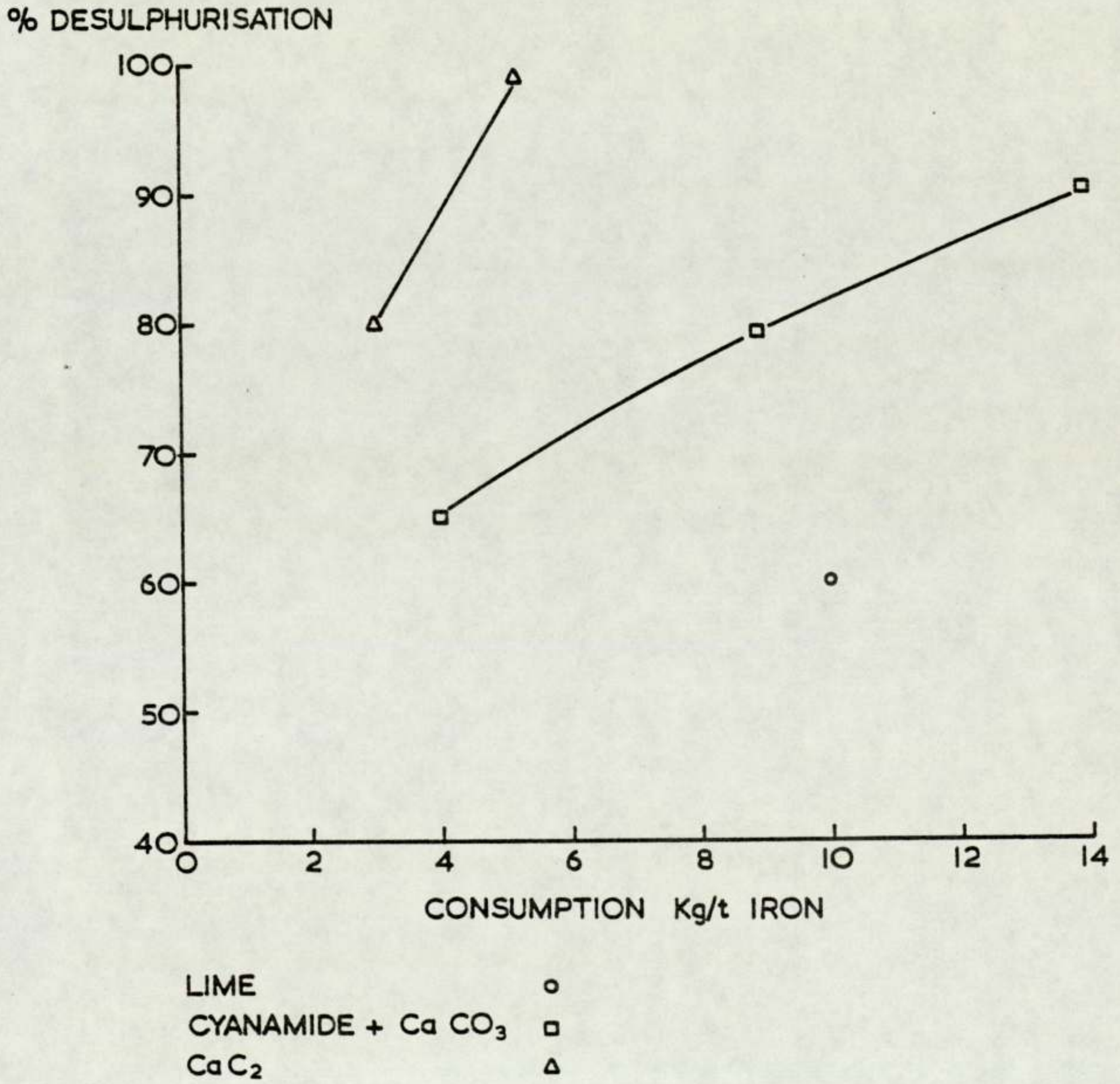


FIG 30

PERCENTAGE DESULPHURISATION VS CAD COMSUMPTION

(TESTS 1 - 129)

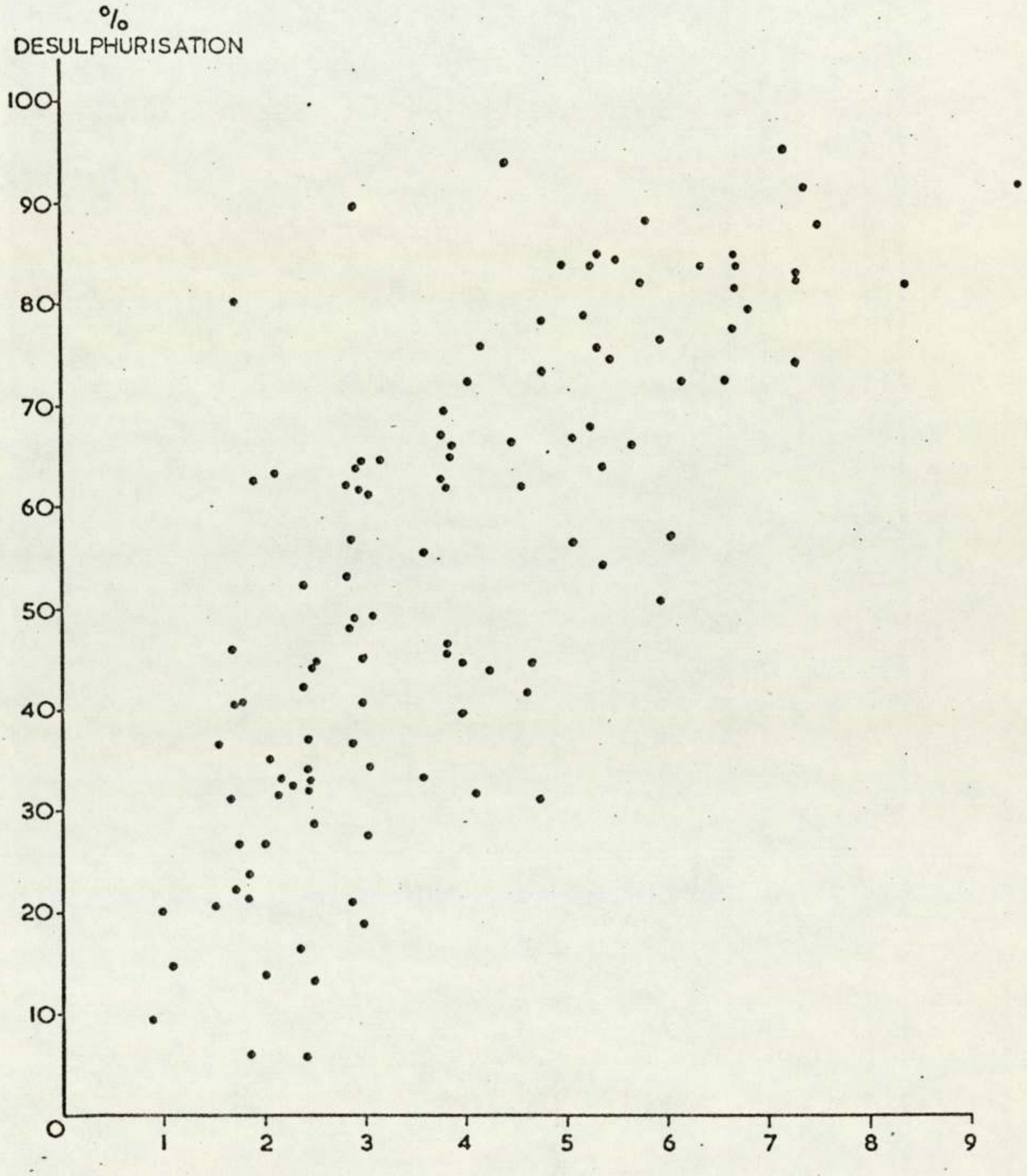


FIG 31

The question of which reagent, has been narrowed down to only a few possible materials, and a mixture based on calcium carbide is almost universally used.

The aim of the following project work has been to examine the validity of the sampling methods used at the Appleby-Frodingham Works to determine the pre-treatment sulphur level for the torpedo treatment plant, and to investigate the factors affecting the degree of mixing of iron obtained during the torpedo and transfer ladle injection processes.

PLANT TRIALS and LABORATORY WORK

PART ONE

DESULPHURISATION IN TORPEDO LADLES

3. TORPEDO SAMPLING TRIALS

3.1.

It is known that the sulphur content of iron can vary during a cast from a blast furnace. The routine sampling practice at the Appleby-Frodingham blast furnace plant is to take duplicate samples at three stages during the filling of a torpedo, i.e. at $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ full. The best quality sample of each pair is analysed and the three analyses averaged to give an overall torpedo analysis. Pre-desulphurisation samples at the plant are taken using a 'lollipop' iron sampler Fig. 32. The sampling device only penetrating the top few inches (about 15 cm) of the liquid iron. At the Appleby-Frodingham Works the larger furnaces normally cast more iron than can be held in a single torpedo, this means that a high proportion of torpedoes are filled with metal from more than one cast or possibly more than one furnace.

3.2.

It was necessary to carry out several trials at the desulphurisation plant under controlled conditions to investigate the limits of operation, and the practical effects of the controllable plant variables, on the process. Any trial under these conditions would have been wasted unless the initial metal sample was representative of the contents of the torpedo. This would also seriously affect normal plant operation.

With this in mind an investigation into the presence of stratification in the torpedo ladles was undertaken. The procedure used was to take samples from a variety of torpedoes using specially developed multi-point sampling probes. The development of a sampling probe and technique took place over a series of short trials.

3.3. Sampler Development

3.3.1. Trial 1

Initially it was decided to test two techniques for multi-level sampling, i.e. simultaneous sampling at different metal depths in the torpedo.

1. Using special immersion samplers to obtain samples from the bottom and centre of a torpedo the top sample being taken with a routine lollipop sampler. The special sampler was a standard hot metal sample pot fitted with a metal cover, the pot and cover being attached to long handles for immersion and sampling, Fig. 33.
2. Using a variant of a melt sampler developed by the Corporate Laboratories of B.S.C., Fig. 34, for sampling steel. This consists of a 2.5 cm diameter steel tube crimped to form a number of sample pods. Each pod is drilled and capped with a suitable material. The sampler itself is attached by screw joints to a handle of sufficient length to enable safe working and ensure ease of sampling. The sampling position was at the end of the blast furnace runner, overlooking the mouth of the torpedo. The minimum overall length of the sampling device for safe working was 14 feet. Since only the practicability of the device was being tested aluminium was used as the sample capping material to ensure that a sample would be taken.

IMMERSION SAMPLER (LOLLIPOP TYPE)

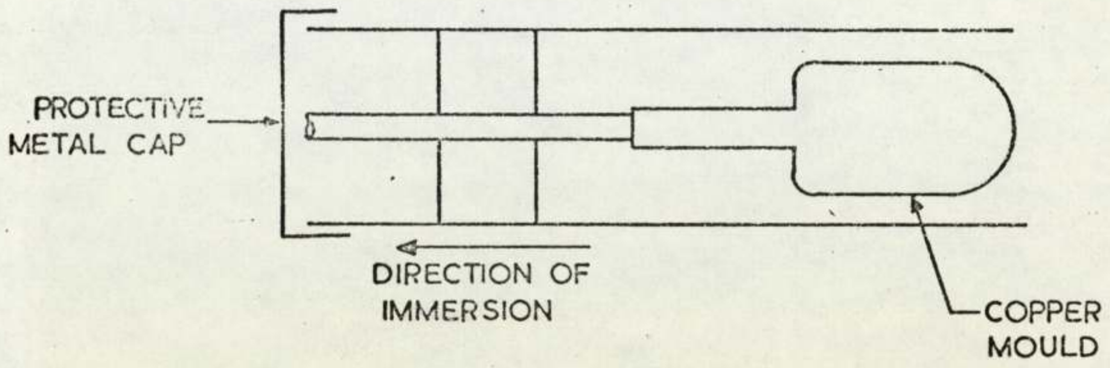


FIG 32

TRIAL (DEEP) IMMERSION SAMPLER

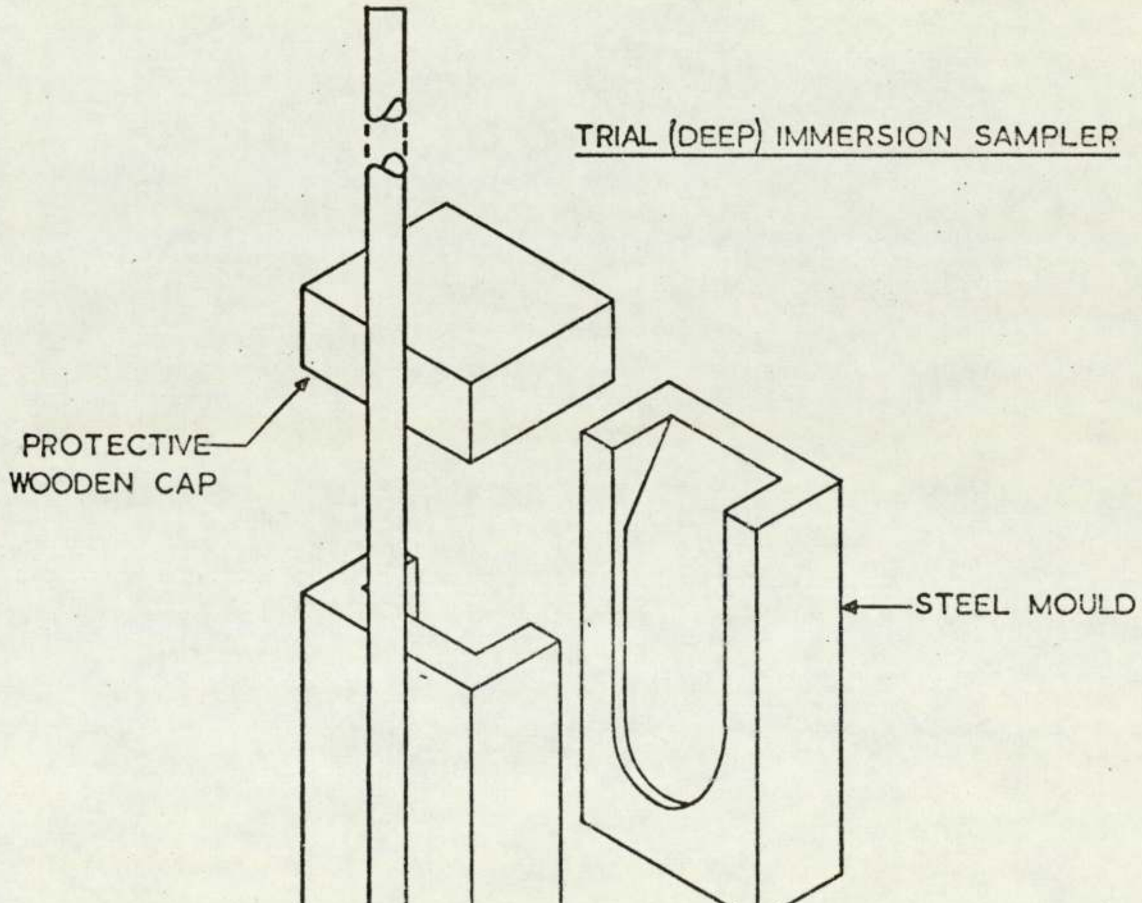


FIG 33

The immersion sampler proved too cumbersome for two people to handle under plant conditions and was not strong enough to resist bending of the handles during the sampling period (5 - 15 secs.) (It was found later that a unit similar to this was used successfully at August Thyssen for routine sampling. Their sampler however was much stronger and hydraulic drives were essential.)

The multi-point samplers took samples in two of the three pipe sections, the upper pod being heavily slagged over. The Samples were removed from the pods by cutting the pipe on a conventional slitting wheel and knocking the iron out with a hammer. The samples had areas of high porosity, and because of the slow cooling rate exhibited marked segregation. In addition as the sample pods passed through the slag layer some slag became mixed with the metal. For these reasons the samples were unsuitable for spectrographic analysis. Analysis for carbon and sulphur was done by a combustion method and wet analysis used for the other elements. The analyses of the samples taken and those for the normal blast furnace runner analyses are shown in Table 6.

3.3.2. Trial 2

The practicability of the multi-point sampler was confirmed by testing three samplers in succession in a single torpedo. The analyses found are shown in Table 7. The cast chosen had consistent analysis from the start to the end of casting, this was reflected in the results. The sample probe proved easy to handle in the confined space available.

TABLE 6

Torpedo Sampling - Trial 1

T.13, Queen Anne Furnace, 30th August 1974, 1.45 p.m.

Blast Furnace Runner Analysis

C	Si	Mn	P	S	
3.75	1.11	.49	.28	.081	
3.65	1.12	.47	.26	.076	
3.85	1.33	.49	.29	.065	
3.75	1.19	.48	.27	.074	Average

Pipe Sample

C	Si	Mn	P	S	Position
3.96	1.16	.44	.25	.075	Bottom
3.94	1.18	.48	.26	.075	Centre

TABLE 7

Torpedo Sampling - Trial 2

Blast Furnace Runner Analysis

C	Si	Mn	P	S
4.36	1.09			.036
4.29	1.07			.038
4.34	1.05			.038

Pipe Sample

	C	Si	S	Position
(1.1)	4.15	1.08	.037	Bottom
(2.1)	3.87	1.04	.039	Bottom
(3.1)	4.22	1.07	.038	Bottom
(1.2)	4.14	1.07	.038	Centre
(2.2)	Unfit for Analysis			-
(3.2)	4.08	1.08	.039	
(1.3)	4.07	1.05	.040	Top
(2.3)	Unfit for Analysis			-
(3.3)	4.3	1.07	.040	

It was evident that immersion time was critical for each of the three sample pods. Aluminium capping was thought to be suitable for the pod with the shortest immersion time.

3.3.3. Trial 3

To ensure valid results it was essential that a reasonable time interval should elapse after the immersion of the sampler to ensure that the sample was taken from the correct position in the torpedo. The sampler was therefore modified to take only a single sample, the molten metal completing an electrical circuit containing a light bulb Fig. 35. This system was used to test several capping materials. As suspected aluminium melted almost immediately and was therefore suitable for the top sample only. For the other sample points mild steel sheet proved the most reliable material, 0.8 mm. thickness being the final choice. This required an immersion time of 6 secs. before a sample was taken, a sufficient period to be certain of reaching the bottom of the torpedo, with some excess time available.

A set of four pipe samplers were made up and tested. In each case the caps melted at the required time. However, the longer immersion times caused the pipes to be so hot that the crimps opened slightly and the molten metal ran through. The sampler was therefore modified to overcome this. Instead of being crimped, the pipe was cut and a 5 cm. length of steel rod 2.5 cm. dia. welded into the pipe, the pipe being rejoined by welding, Fig. 36. This new design performed satisfactorily and was used on all future trials. Results from the final test cast are in Table 8.

MULTIPOINT SAMPLER

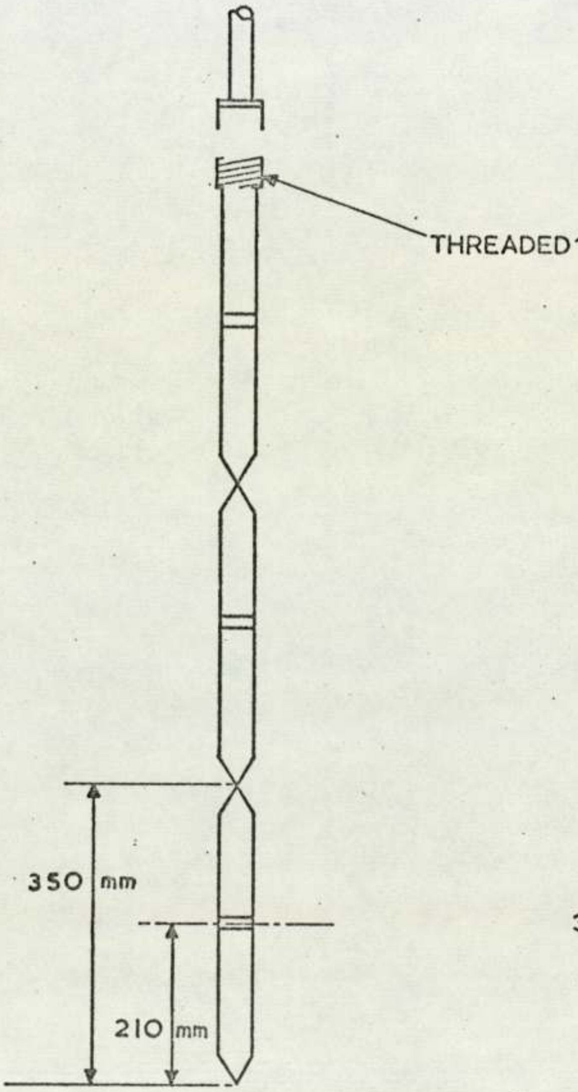


FIG 34

MULTIPOINT PIPE SAMPLER

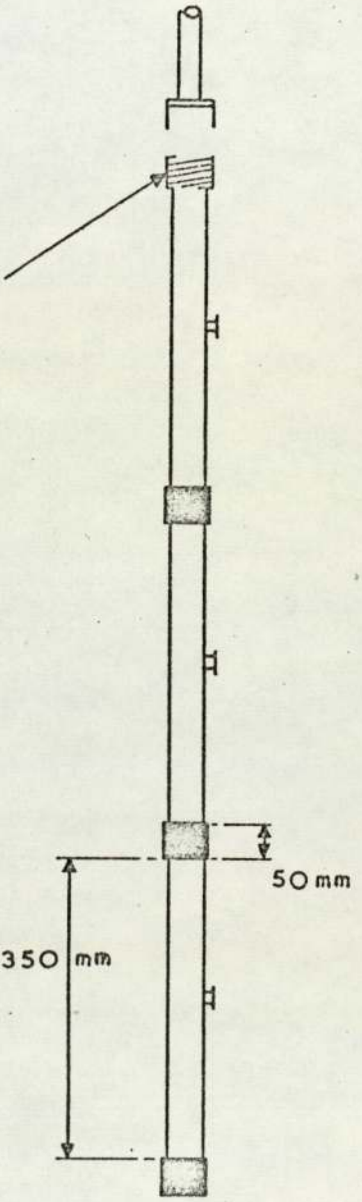


FIG 36

TEST SAMPLER

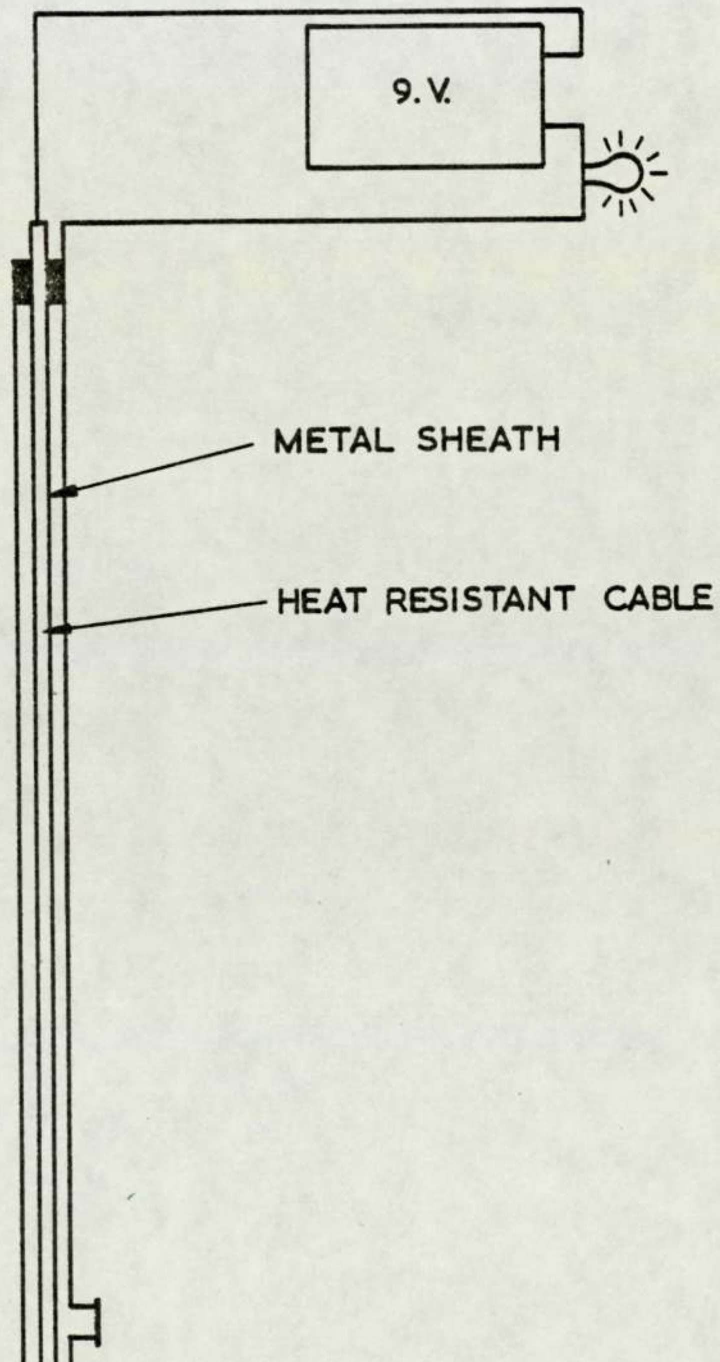


FIG 35

3.4 Ladle Stratification Trial

3.4.1.

Having proved the success of the multi-point sampler a plant trial was undertaken to investigate the presence of stratification and the existence of a difference between the iron analysis at the blast furnaces and that at the desulphurisation plant.

3.4.2. Trial Procedure

1. At the blast furnaces samples were taken from the runner at five minute intervals during casting, in addition to the routine samples. Samples were taken from the torpedo as follows:

   a) Immersion (lollipop type) metal samples from the full torpedo.

   b) Samples from the bottom, centre and top metal levels with the multi-point sampler.

   c) Slag samples both before and after filling.

2. At the desulphurisation plant, immersion, multi-point and slag samples were taken both before and after desulphurisation.

3.4.3. Accuracy of Analysis

Analysis differences in this type of trial can be very misleading unless the accuracy of the analytical method is known. An examination of iron analysis accuracy was therefore carried out at the author's request at the Redbourn Works laboratories. Samples were used from a sampling trial in the current series.

The results gave the following average standard deviations for four slab type samples, each sparked ten times on a Polyvac machine. The results are applicable to any single analysis result.

	C	Si	Mn	P	S
s.d.(±%)	0.11	0.011	0.0055	0.0048	0.0027

Routine analysis is normally based on the average result of two samples each sparked twice, this means that for that average the following 95% confidence limits apply.

	C	Si	Mn	P	S	
±%	0.16	0.016	0.0078	0.0068	0.0038	for two sparks
±%	0.11	0.011	0.0055	0.0048	0.0027	for four sparks

Similar accuracy figures were quoted for the chemical analysis methods used.

Poor sample quality however causes the rapid deterioration of spectrographic analysis accuracy, and another major problem with hot metal samples is the presence of free graphite. If the spark picks this up then the percentage sulphur recorded will also be higher than actual. For this reason, only the chemical analysis results obtained were examined for trial purposes.

Slag analysis is accurate to less than ± 0.5% for the major constituents, and should therefore cause no problem in data interpretation.

TABLE 8

Final Test Cast

T.2, Queen Mary, 25th April, 3.00 p.m.

Blast Furnace Runner Analysis			Multi point Sampler			
C	Si	S	C	Si	S	Position
3.80	.72	.083	3.99	.72	.087	Top
3.88	.76	.079	3.63	.58	.078	Bottom

TABLE 9

Torpedo Draining Times

Torpedo No.	Test Cast	Drained	Tare t.	Slag plus Skull (approx) t.
9	1220	New Torpedo	197	Nil
14	0930	0820	218	21
5	1120	0930	233	36
5	0940	0600	216	19

3.5. Trial Results and Discussions

Four torpedoes were tested, the results are given in Tables 9 - 14 with notes on the torpedo slag content and the torpedo tare weights and slag build up.

3.5.1. Trial 4 (Table 11)

a) The special runner samples analysed decreased during the cast from 0.066% to 0.058%S the average result being 0.004% higher than the figure obtained by routine sampling and analysis.

b) The immersion samples taken at the blast furnace were higher in sulphur than the average runner analysis. The shallow immersion sample was also 0.01%S higher than the corresponding sample at the desulphurisation plant, but agreed closely with the routine sample at that plant.

c) The difference between post desulphurisation samples is 0.012%S. This would be critical in calculating the desulphurisation efficiency.

d) The routine analysis would indicate a rise in the sulphur content of 0.009% as the iron transferred from the blast furnaces to the desulphurisation plant. However the duplicate sample taken at the desulphurisation plant agreed closely with both the routine and special runner average analyses indicating that no change had in fact taken place.

3.5.2. Trial 5 (Table 12)

a) The special runner samples decreased from 0.064% to 0.056%S. The average was again 0.004% higher than the routine figure.

b) There was only marginal agreement between the analyses of samples taken from the torpedo, both at the blast furnaces and at the desulphurisation plant (range 0.007%). It is noticeable however that the routine desulphurisation plant sample gave the lowest %S, 0.047.

c) The three samples taken after desulphurisation range from 0.016% to 0.030%S.

d) Special runner samples 1a and 1b were taken from the same sample spoon. The differences in analyses are quite large 0.09%C and 0.005%S.

e) The routine analyses suggest a drop in percentage sulphur of 0.007 which is substantiated by the special samples although the initial and final levels are different.

3.5.3. Trial 6 (Table 13)

a) The special runner samples decreased from 0.116% to 0.088%S. The difference of the average from the routine figure was 0.010%S.

b) All other samples were taken from the upper levels of metal and showed good agreement, except for the multi-point sampler which gave a top metal figure of 0.090% - close to the routine runner sample result.

c) The routine analyses indicated a rise in sulphur level of 0.009% which was not supported by the other results.

3.5.4. Trial 7 (Table 14)

The metal was very consistent throughout the cast with no variation in average sulphur analyses at the blast furnaces and little difference between the sulphur content of any samples taken later.

3.5.5. Discussion of Trials

The results do not suggest that any significant change in metal %S takes place between the blast furnaces and the desulphurisation plant. Where changes in sulphur are indicated by the routine results, the special samples suggest that sampling techniques and sample quality may be at fault. The major differences are with the desulphurisation plant results since these are taken from a single sample, of the immersion type. There is some evidence gained from visual examination of the polished samples, that sufficient slag can be trapped in the sample to affect the analysis. The blast furnace runner results gave the most representative analysis of the cast as long as the samples were taken at the correct intervals relative to the weight of metal cast.

The results gave no evidence of stratification in the torpedo lades. Experiments in a torpedo model carried out in conjunction with this trial showed that good mixing should be obtained (except perhaps at the extremities of the torpedo) as long as the casting rate is reasonably high and marked changes in analysis do not take place near the end of the cast when the torpedo is almost full.

The slag samples were difficult to obtain and in all cases were contaminated by iron. The change in slag analysis as sampled at the blast furnaces and desulphurisation plant was quite large in the last three trials. In each case there was some residual slag in the torpedo before filling and was mainly of the type formed during desulphurisation. The analyses would indicate that this slag "floats" on top of the fresh blast furnace slag from the current fill of metal. This makes any calculation on change in metal chemistry based on slag analysis impossible.

For any performance trials to be conducted at the desulphurisation plant, the best estimate of initial sulphur level would be based on special samples taken from the blast furnace runner. In practice these could not be taken because of manning difficulties, and the before treatment sulphur was based on a sample taken at the desulphurisation plant before injection began.

TABLE 10

Torpedo Slags

Trial 4	No slag measurable on torpedo after casting at blast furnaces.
Trial 5	10 cm slag in torpedo before casting.
Trial 6	30 cm slag in torpedo before casting, mainly desulphurisation product. Became viscous by end of cast.
Trial 7	Desulphurisation product slag in lump form 10 - 12.5 cm thick before casting. The layer became more even by the end of cast.

TABLE 11

TORPEDO SAMPLING - TRIAL 4

	Analysis							
	Special Samples (Chemical)			Routine Samples (Polyvac				
Sample	C	Si	S	C	Si	Mn	P	S
Runner Samples 1	4.07		.066	4.25	1.14	.52	.26	.061
2	4.09		.064	4.35	1.14	.52	.26	.057
3	4.18		.058	-	1.13	.49	.26	.054
4	4.20		.058					
5	4.29		.058					
Average Runner Sample	4.17		.061	4.30	1.14	.51	.26	.057
Shallow Immersion Samples	4.12		.068					
Deep Immersion Samples	4.19		.063					
D/S Plant Samples								
Immersion before	4.17		.058					.066
Immersion after	4.17		.014					.002

Slag Analyses

	CaO	SiO_2	Al_2O_3	S	C_{total}	CO_2
At Blast Furnace	No slag on ladle					
Pre D/S *	0.3	47.3	18.6	.035		
Post D/S *	12.8	2.6	1.0	.680	13.8	.4

* Bulk of remainder of sample was iron shot

TABLE 12

TORPEDO SAMPLING - TRIAL 5

Sample	Analysis							
	Special Samples (Chemical)			Routine Samples (Polyvac)				
	C	Si	S	C	Si	Mn	P	S
Runner Samples 1a	4.04		.064	–	.94	.43	.26	.056
1b	4.12		.058					
2	4.09		.056	4.24	.91	.43	.26	.055
3	4.12		.056	4.40	.91	.43	.26	.051
4	4.11		.057					
5	4.18		.058					
Average Runner Sample	4.12		.058	4.32	.92	.43	.26	.054
Multipoint Samples								
Avg. of 2 (bottom)	3.46	.68	.049					
Avg. of 1 (top)	3.89	.80	.052					
D/S Plant Samples								
Immersion before	4.09		.054					.047
Immersion after	4.10		.030					.020
Multipoint Samples								
before avg. of 2								
(centre)	3.78	.79	.051					
(top)	3.84	.82	.052					
After top	3.83	.80	.016					

Slag Analyses

	CaO	SiO_2	Al_2O_3	S
At Blast Furnaces	18.8	64.3	3.5	.48
Pre D/S *	24.1	16.7	1.2	1.05
Post D/S *	23.3	23.9	1.2	1.47

* Bulk of remainder of sample was iron shot

TABLE 13

TORPEDO SAMPLING - TRIAL 6

Sample	Analysis							
	Special Samples (Chemical)			Routine Samples (Polyvac)				
	C	Si	S	C	Si	Mn	P	S
Runner Samples 1	3.97		.116	4.05	.64	.44	.28	.108
2	3.97		.114	4.10	.68	.45	.29	.090
3	4.07		.102	4.10				
4	4.10		.088					
Average Runner Sample	4.03		.105	4.83	.71	.46	.29	.095
Shallow Immersion	4.04		.105					
Deep Immersion	4.11		.104					
Multipoint Sample (top)	3.98	.70	.090					
D/S Plant Samples								
Immersion shallow	4.08		.104					
Immersion deep	4.04		.103					
Multipoint (top)	4.04	.67	.104					

Slag Analysis

	CaO	SiO_2	Al_2O_3	S	C_{total}	CO_2
At Blast Furnaces (1)	32.4	32.7	8.5	1.05		
(2)	38.1	36.7	7.7	1.10		
D/S Plant Powder	48.9	2.5	.6	.76	6.6	1.7
Lump *	41.9	2.9	.5	.75	12.6	1.1

* Bulk of remainder of sample was iron shot

TABLE 14

TORPEDO SAMPLING - TRIAL 7

	Analysis							
	Special Samples (Chemical)			Routine Samples (Polyvac)				
Sample	C	Si	S	C	Si	Mn	P	S
Runner Samples 1	4.20		.038	4.51	1.11	.53	.25	.035
2	4.31		.042	4.29	1.08	.53	.27	.034
3	4.29		.044	4.08	1.06	.56	.27	.037
4	4.28		.034					
5	4.29		.035					
6	4.22		.033					
7	4.19		.045					
Average Runner Samples	4.25		.038	4.29	1.08	.54	.26	.035
Immersion Shallow	4.28		.040					
Immersion Deep	4.28		.036					
Multipoint Sample								
Avg. of 2, Bottom	3.65	.89	.036					
Top	3.90	.98	.036					
D/S Plant Samples								
Immersion Shallow	4.28		.037					
Immersion Deep	4.28		.037					
Multipoint Sample avg. of 2								
Bottom	3.81	.94	.036					
Centre	3.80	.94	.036					
Top	3.80	.99	.037					

Slag Analysis

	CaO	SiO_2	Al_2O_3	S	C_{total}	CO_2
At Blast Furnaces (before cast)	32.4	25.4	1.8	1.25		
At Blast Furnaces (at end cast)	40.7	26.8	3.2	1.69		
At D/S Plant (1) **	47.1	6.5	1.6	1.60	10.8	.7
(2) **	34.1	2.0	.2	4.00*	11.5	.9

* checked at 3.98 ** Bulk of remainder of sample was iron shot.

4. SIMULATION OF HOT METAL FLOW PATTERNS IN A TORPEDO DURING INJECTION

4.1.

It has been shown (section 2.3) that one of the major factors in determining the efficiency of desulphurisation is the transport of sulphur to the reaction zone, i.e. the degree and efficiency of mixing of the metal in the torpedo. A series of experiments has been made, using a twelfth scale model of a torpedo, to investigate the flow patterns set up during injection and the effects of plant variables such as gas/material delivery rate, lance angle and position.

The model itself, was built from perspex, the main body being joined to the ends by metal flanges for strength. Fig. 37.

4.2. Use of a Model for Flow Simulation

4.2.1. Similarity

In order to obtain a complete and accurate representation of the metal flow in a torpedo the model should be similar in all respects. The various types of similarity are defined as follows:

1) Two bodies are geometrically similar when to every point in the one body there exists a corresponding point in the other.

2) Geometrically similar moving systems are kinematically similar when corresponding particles trace out geometrically similar paths in corresponding intervals of time.

TORPEDO MODEL

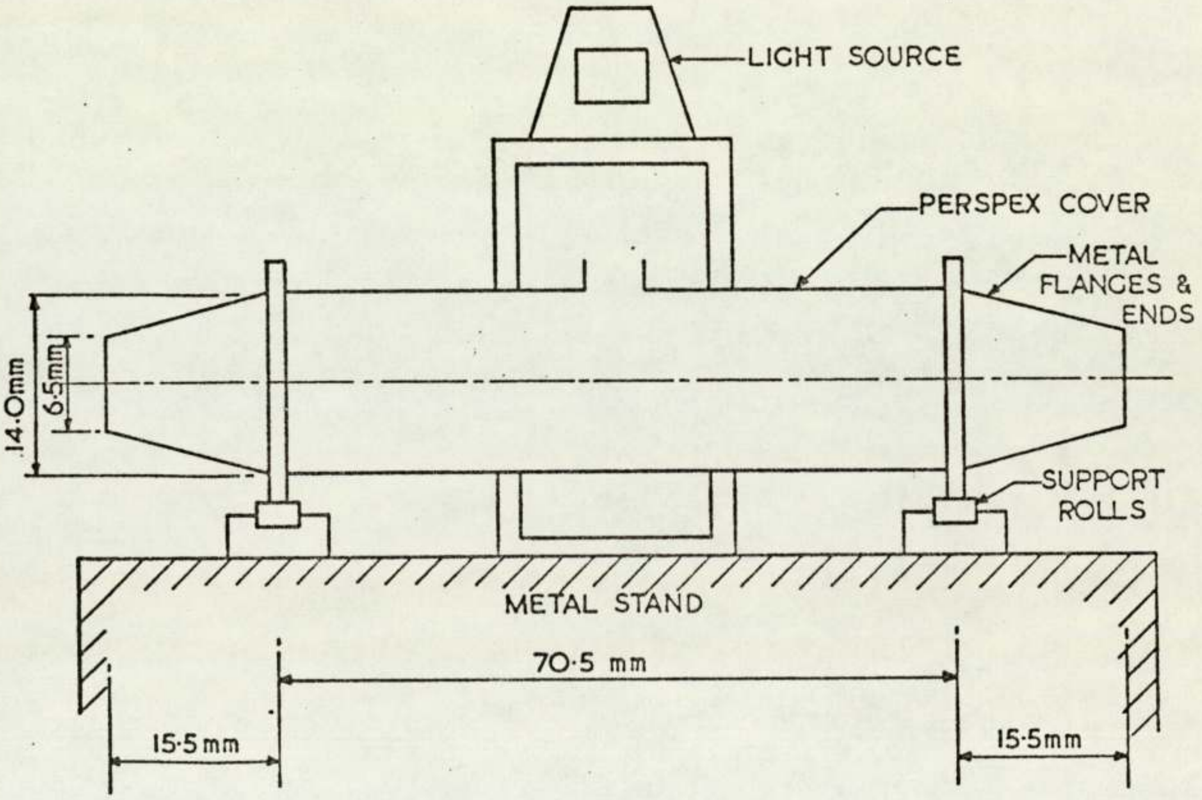


FIG 37

3) Geometrically similar moving systems are dynamically similar when the ratios of all corresponding forces are equal.

4) Geometrically similar systems are thermally similar when corresponding temperature differences bear a constant ratio to one another and when the systems if moving are kinematically similar.

5) Geometrically and thermally similar systems are chemically similar when corresponding concentration differences bear a constant ratio to one another and when the systems if moving are kinematically similar.

In this case the model should ideally exhibit geometric, kinematic and dynamic similarity.

Similarity Criteria are ratios of like quantities used to determine model dimensions and operating conditions.

1) When the differential equations that govern the behaviour of the system are unknown, and all the variables are known dimensionless analysis may be used.

2) Where the differential equations are known but cannot be integrated the criteria can be derived from the equations.

When the equations are known and calculable there is no need for model work.

4.2.2. Dimensionless Analysis of the System

The variables influencing the flow of metal in a torpedo are:

Velocity	V
Viscosity	μ
Density	ρ
Length	L
Gravity	g
Surface Tension	σ

The relationship between these variables may be expressed as a function of

$$(V^a \; \mu^b \; \rho^c \; L^d \; g^e \; \sigma^f) = 0$$

i.e. a function of $\left(\frac{L}{t}\right)^a \left(\frac{M}{Lt}\right)^b \left(\frac{M}{L^3}\right)^c L^d \left(\frac{L}{t^2}\right)^e \left(\frac{M}{t^2}\right)^f = 0$

Applying the condition of dimensional homogeneity, the following must be true

$$b + c + f = 0$$

$$a - b - 3c + d + e = 0$$

$$-a - b - 2c - 2f = 0$$

$$\therefore \; (V^{b + 2e + 2f}) \; \mu^{-b} \; (\rho^{b + f}) \; (L^{b + f - e}) \; g^{-e} \; \sigma^{-f} = 0$$

which gives $\left(\frac{V \; L}{\mu}\right)^b \left(\frac{V^2}{Lg}\right)^e \left(\frac{V^2 \rho \; L}{\sigma}\right)^f = 0$

or a function of $\left(\frac{V \; L}{\mu}, \; \frac{V^2}{Lg}, \; \frac{V^2 \rho \; L}{\sigma}\right) = 0$ (4.1)

i.e. the flow is a function of the Reynolds, Froude and Weber numbers, respectively.

4.2.3.

These parameters may be equated between the model and the plant to determine the scale functions to be applied.

Equating the Weber and Froude Numbers

$$\frac{\rho_m \; V_m^2 \; L_m}{\sigma_m} = \frac{\rho_p \; V_p^2 \; L_p}{\sigma_p} \quad \text{and} \quad \frac{V_m^2}{L_m g} = \frac{V_p^2}{L_p g}$$

where m, denotes model - values below for model and water at 15°C - and p, plant values - values for torpedo, and iron at 1350°C.

i.e. $\frac{1 \times 10^3 \; V_m^2 \; L_m}{6.4 \times 10^{-2}} = \frac{6.4 \times 10^3 \; V_p^2 \; L_p}{1.47}$ and $\frac{V_m^2}{V_p^2} = \frac{L_m}{L_p}$

$$\therefore \quad \frac{10^3 \; L_m}{6.4 \times 10^{-2} \; L_p} \; L_m = \frac{6.4 \times 10^3 \; L_p}{1.47}$$

$$\therefore \quad \frac{L_m^2}{L_p^2} = \frac{6.4 \times 10^3 \times 7.5 \times 10^{-2}}{1.47 \times 10^3} = \underline{32.65 \times 10^{-2}}$$

$$\therefore \quad \frac{L_m}{L_p} = 0.57 \qquad (4.2)$$

and $\frac{V_m}{V_p} = 0.756$

Equating the Weber and Reynolds Numbers

$$\frac{\rho_m \; V_m^2 \; L_m}{\sigma_m} = \frac{\rho_p \; V_p^2 \; L_p}{\sigma_p} \quad \text{and} \quad \frac{L_m \; V_m \; \rho_m}{\mu_m} = \frac{L_p \; V_p \; \rho_p}{\mu_p}$$

i.e. $\frac{L_m}{L_p} = \frac{\rho_p \; V_p^2 \; \sigma_m}{\sigma_p \; \rho_m \; V_m^2}$ and $\frac{V_m}{V_p} = \frac{L_p \; \rho_p \; \mu_m}{\mu_p \; L_m \; \rho_m}$

$$\therefore \quad \frac{L_m}{L_p} = \frac{\rho_p \; \sigma_m}{\sigma_p \; \rho_m} \times \frac{\mu_p^2 \; L_m^2 \; \rho_m^2}{L_p^2 \; \rho_p^2 \; \mu_m^2} = \frac{L_m^2 \; \sigma_m \; \rho_m \; \mu_p^2}{L_p^2 \; \sigma_p \; \rho_p \; \mu_m^2}$$

$$\frac{L_p}{L_m} = \frac{7.5 \times 10^{-2} \times 10^3}{1.47 \times 6.4 \times 10^3} \frac{\mu_p^2}{\mu_m^2} = 0.797 \; \frac{\mu_p^2}{\mu_m^2} \times 10^{-2}$$

For water and iron $\frac{\mu_p^2}{\mu_m^2} = \frac{(7.5 \times 10^{-3})^2}{(0.75 \times 10^{-3})^2} = 100$ (at 35°C) (or 110 at 15°C)

$$\therefore \quad \frac{L_m}{L_p} = 0.797 \qquad (4.3)$$

Equating the Reynolds Number only

$$\frac{L_m}{L_p} = \frac{V_p \rho_p \mu_m}{V_m \rho_m \mu_p}$$

with a model linear scale of 1/12th

$$\frac{1}{12} = \frac{V_p}{V_m} \times \frac{6.4 \times 10^3}{10^3} \times \frac{0.75}{7.5}$$

$$\therefore \frac{V_p}{V_m} = \frac{1}{7.68} \quad \text{i.e.} \quad V_m = 7.68 \ V_p \qquad (4.4.)$$

Equating the Weber and Froude Numbers gives a linear parameter $\frac{L \text{ model}}{L \text{ plant}} = 0.57$ if water is to be used as the model fluid. With an actual torpedo length of 12.6 m. the length of a model scaled on these parameters was prohibitive for laboratory work (7.2 m.). The Weber and Reynolds Nos. if equated give a linear ratio of 0.80, with a similar conclusion. Since metal flow was the prime parameter being considered maintenance of similarity based upon Reynolds number alone is reasonable; in this instance giving $\frac{V \text{ plant}}{V \text{ model}} = \frac{1}{7.7}$ (defining Re as $\frac{LV\rho}{\mu}$) i.e. fluid velocity in the model should be 8.6 times that on the plant. At this time the plant flow velocities are not known.

A similar single parameter approach in the choice of modelling criteria based on energy input has been used successfully to model large scale steel plant phenomena. This method has been used for this work. (ref. 64).

The criterion, is that the rate of energy supply per unit mass of liquid should be the same for the model and the plant i.e. the ratio of the rates of energy supply to the model and plant to be equal to the corresponding ratio of liquid masses.

4.3 Modelling Parameters

4.3.1. Plant Conditions

The first step is to calculate the rate of energy supply to the metal, (ref. 64).

Plant Conditions assumed are:

Transport gas rate	0.8 N_m^3/min
Desulphurising agent rate	80 kg/min
Lance immersion depth	1.75 m.
Metal temperature	1350°C
Lance diameter	0.0254 m.

Considering the transport gas alone.

The rate of supply of kinetic energy is

$$= \tfrac{1}{2}\,\rho\,Q\,V^2 = \tfrac{1}{2}\,\rho\,Q\,\left(\frac{Q}{A}\right)^2$$

$$= 0.5 \times 5.2 \times 0.0028 \left(\frac{0.0028}{0.000506}\right)^2 = 0.23 \text{ watts} \qquad (4.5)$$

The rate of supply of potential energy has been calculated in two ways, (ref. 65), the first based directly on the volume of metal moved by the rising gas, the second based on the work done by the gas as it rises through the metal, i.e. where h = metal depth, x = distance bubble rises through metal.

1.

$$\int_{v_x = 0}^{v_x = h} v_x = v_N \frac{\pi}{\pi + \rho g x}\, dx \qquad (4.6)$$

$$= v_N \pi / \pi + \rho g x$$

and 2.

$$\int_{x = 0}^{x = h} F \; dx = \int_0^h P \, dv$$

The volume of gas in the iron $v = \dfrac{v_N}{\pi + \rho g x}$

$$\therefore \quad dv = \frac{-v_N \pi \rho g}{(\pi + \rho g x)^2} dx$$

$$\therefore \int_{x=0}^{x=h} p \, dv = -\pi \rho g v_N \int_{x=0}^{x=h} \frac{dx}{(\pi + \rho g x)}$$

$$= -\pi \rho g v_N \cdot \frac{1}{\rho g} \Big[\ln (\pi + \rho g x) \Big]_0^h$$

$$= \pi v_N \ln \left(1 + \frac{\rho g h}{\pi} \right) \qquad (4.7)$$

The latter is the more rigorous treatment and as such has been used in this work.

The rate of supply of potential energy, neglecting temperature rise effects, is therefore

$$2.11 \times 10^5 \times 0.0133 \ln \left(1 + \frac{6400 \times 9.81 \times 1.75}{2.11 \times 10^5} \right)$$

$= 1176.4$ watts

Hence the effect of kinetic energy on the system is negligible.

Assuming that the gas reaches the metal temperature by the time it reaches the surface, then the average gas temperature may be taken as $\dfrac{273 + 1623}{2} = 948^{\circ}K$

Therefore the actual rate of energy, input by the carrier gas is $1176 \times \dfrac{948}{273} = 4085$ watts.

The major source of energy in the process is the gas released by the decomposition of the calcium carbonate. An overall feed rate of 80 kg/min gives 0.312 kg/sec of carbonate. Assuming 100 per cent decomposition at $825^{\circ}C$ and that it is released instantaneously at the lance exit, the rate of supply of energy, from 0.281 m^3/sec gas, is

$$2.11 \times 10^5 \times 0.281 \times \ln \left\{1 + \frac{6400 \times 9.81 \times 1.75}{2.11 \times 10^5}\right\}$$

= 24858 watts

4.3.2. Model Operating Values

The model linear scale is $1/12 = \frac{L_m}{L_p}$

The rates of energy supply are to be the same

$$\therefore \quad \frac{U_m}{t_m \ M_m} = \frac{U_p}{t_p \ M_p} \qquad (4.8)$$

$$\text{i.e.} \quad \frac{(U_m)}{(t_m)} \Big/ \frac{(U_p)}{(t_p)} = \frac{M_m}{M_p}$$

$$\text{and} \quad \frac{M_m}{M_p} = \frac{\rho_m \ L_m^3}{\rho_p \ L_p^3} = \frac{\rho_m}{\rho_p} \left\{\frac{L_m}{L_p}\right\}^3$$

$$= \frac{1}{6.4} \left\{\frac{1}{12}\right\}^3$$

$$= 0.0000904$$

$$= \frac{1}{11100}$$

Therefore the rate of energy supply to the model should be

1) For the carrier gas 0.369 watts

2) For the carbonate decomposition 2.248 watts.

The required model gas rates are, by substitution in equation (4.7).

1) For the carrier gas

$$\frac{0.369}{101325 \ \ln \left(1 + \frac{1000 \times 9.81 \times 0.146}{101325}\right)}$$

$$= 0.0174 \ N_m^3/\text{min}$$

Similarly 2) For the carbonate decomposition

Model gas rate = 0.0948 N_m^3 /min

i.e. Total model gas rate = 112.2 l/min

The assumption is made that the carbonate particles reach decomposition temperature almost instantaneously.

If contact resistance between the particle and the metal can be neglected, then the centre point temperature of a sphere suddenly immersed in a fluid may be determined at any immersion time (t) by

$$T = Ts + (T_i - T_s) \times f_2 \left(\frac{4 \alpha t}{L^2}\right) \qquad \text{(ref.66)}$$

where in this instance $Ts = 1350^{\circ}C$

$\rho = 169.25 \text{ lb/ft}^3$ (2.711 gm/cc)

$Ti = 25^{\circ}C$

$T = 825^{\circ}C$ (decomposition temperature)

$\alpha = {}^{K}/Cp$

$$Cp = 24.98 + 5.24\, T \times 10^{-3} - 6.2 \times 10^5/T^2 \text{ at } 400^{\circ}C$$

$$= 29.875 \text{ cal}/^{\circ}/\text{mole} = 0.2988 \text{ Btu/lb}^{\circ}F$$ [illegible]

$$K = 1.3 \text{ Btu/hr ft}^2\ {}^{\circ}F/\text{ft}$$

$$L = 0.125 \text{ mm max}^m, = 0.00041 \text{ ft}$$

$$\therefore \frac{4 \alpha t}{L^2} = \frac{4 \times 1.3 \times t}{0.2988 \times 169 \times 0.00041^2} = 612{,}588 \times t$$

$$(Ts - T)/(Ts - Ti) = (2462 - 1517)/(2462 - 77)^{\circ}C = 0.396$$

Using the cooling/heating curves in Kern

$$\frac{4 \alpha t}{L^2} = 0.16$$

$$\therefore t = \frac{0.16}{612{,}588} = 2.612 \times 10^{-7} \text{ hr}$$

$$= 9.4 \times 10^{-4} \text{ sec}$$

If it is considered that a gas shield is formed immediately around the particle then the temperature of its surroundings is limited to 825°C, the decomposition temperature. This increases the heating time for the remaining particle to 0.4×10^{-2} sec. In either case the time is negligible (ref. 67) and the assumption stands. The actual process of particle decomposition and reaction at the lance exit and the interactions with bubble formation and flow are not included in the scope of this thesis.

4.3.3. Estimation of Mixing Times

The modelling criterion can be used to obtain the relationship between the plant and model mixing times. Since all the energy of the gas can be regarded as being transferred to the liquid

$$\tfrac{1}{2} \left(\frac{MV^2}{tM}\right)_m = \tfrac{1}{2} \left(\frac{MV^2}{tM}\right)_p$$

$$\therefore \quad \left(\frac{V^2}{t}\right)_m = \left(\frac{V^2}{t}\right)_p$$

$$\text{i.e.} \quad \left(\frac{LM^2}{t^3}\right)_m = \left(\frac{LM^2}{t^3}\right)_p$$

$$\therefore \quad \frac{t_m}{t_p} = \left(\frac{L_m}{L_p}\right)^{\frac{2}{3}} = \left(\frac{1}{12}\right)^{\frac{2}{3}} = 0.191$$

Therefore mixing times measured on the model should be multiplied by 5.24 to give the plant value.

4.3.4. Model Lance Diameter

The modelling theory assumes a negligible contribution to the mixing forces by the kinetic energy released at the lance exit. Within the limits of the model size the lance diameter was chosen to satisfy this criterion. As will be discussed later the model could not be operated at the maximum theoretical flow rate 112.2 l/min, therefore by example for a model flow of 60 l/min.

$$\text{Model K.E.} = \tfrac{1}{2}\ MV^2 = \tfrac{1}{2}\rho\,\frac{Q^3}{A^2}$$

$\therefore$ For K.E. $\leqslant$ 10% of P.E.

$$A \geqslant \left(\frac{1.251 \times Q^3}{2 \times 0.138}\right)^{\frac{1}{2}} = 0.000067\ m^2$$

$$\text{i.e. Lance diameter} \quad \left(4 \times \frac{0.000067}{\pi}\right)^{\frac{1}{2}}$$

$$= 0.9\ \text{cm}$$

4.3.5. Variation in Assumed Standard Values

The effects of changes in the assumed standard plant operating values on the model gas flow rate are shown in Table 15. The most significant variable is the lance immersion depth. This is of particular interest when the operating problems of torpedo filling level and torpedo bottom skulling are considered.

TABLE 15

Effect of Variation in Operating Values on Model Gas Rate

Reagent Rate kg/min	Immersion m.	Plant P.E. from reagent w.	Model P.E. from reagent w.	Total Model Gas Flow l/min
80	0.7	10789.6	0.9753	58.6
70		9445.7	0.8539	53.5
60		8101.8	0.7324	48.3
80	1.0	14938.6	1.3504	74.4
70		13077.9	1.1822	67.3
60		11217.2	1.0140	60.3
80	1.25	18299.7	1.6543	87.2
70		16020.4	1.4482	78.6
60		13741.0	1.2422	69.8
80	1.75	24858.2	2.2472	112.2
70		21761.9	1.9673	100.4
60		18665.7	1.6874	88.6

Carrier Gas Rate = 0.0133 m^3/sec

Carrier Gas Plant P.E. = 4085 w

Carrier Gas Model Rate = 17.4 l/min

5. PRACTICAL WORK USING THE TORPEDO MODEL

5.1. Introduction

Previous work has shown the importance of vessel shape and metal agitation with respect to the performance of desulphurisation processes. The examination of metal flow patterns, mixing efficiency and the factors affecting them are not readily amenable to plant trials. Some data are obtainable using radio active tracer techniques, but for a torpedo ladle this would require samples to be taken along its length, especially at the ends. The use of a model overcomes these difficulties, allowing multiple trials for any set of conditions and giving a better visual appreciation of the system.

The factors examined using the model are:-

1. Metal flow patterns, affect of a) lance angle
   b) gas rate
2. Metal mixing times, affect of a) lance angle
   b) gas rate
   c) lance immersion depth

   on the time for homogenisation of the melt.
3. The influence of torpedo internal skulls

5.2. Metal Flow Patterns

The degree of mixing within the torpedo is primarily dependent on the rate of gas evolution from the desulphurising reagent. However the angle of inclination of the lance or changes in the lance design determine the position in the torpedo where this energy is released.

5.2.1. Procedure

The flow patterns of the metal were examined using partially expanded polystyrene beads as tracers. In all the tests the position at which the lance passed through the liquid surface and the immersion depth were kept constant. This caused the lance exit to be at different points relative to the torpedo centre (as would occur in practice), for each lance angle or type.

The pattern of flow established in the model was examined at three lance angles (including vertical), and at each angle the gas rate was varied. The test conditions are summarised below, and include a series with a vertical twin nozzle lance.

TABLE 16

TORPEDO MODEL TEST CONDITIONS

Lance Position	Gas Rate (l/min.)
Inclined 70° to horiz.	30, 40, 50
Inclined 50° to horiz.	30, 40, 50
Vertical, single nozzle	9.5*
Vertical, twin nozzle	23*

* maximum rate possible

5.2.2. Results

When using the inclined lance it was found that the gas rates calculated for immersion depths of 1.75 m., i.e. a full torpedo, could not be used because of excessive splashing. The maximum flow rate used, 50 l/min., was that which just avoided splash paralleling the plant situation.

The flow pattern produced is symmetrical about the lance exit. Thus as the gas rate is reduced, at constant lance angle, a dead zone of metal is produced at the torpedo end away from the lance, Figs. 38-40). Reductions in lance angle produce the same effect, Figs. 41-43. At the maximum angle, (70°), and flow rate (as used on plant) this dead zone was not apparent, Fig. 40.

The results suggest that a vertical centrally positioned lance would produce the best results with respect to mixing, at a minimum gas rate. However the rate of gas evolution is such that the lance exit needs to be within the body of the torpedo to avoid splashing. The maximum gas rate was reduced to 9.5 l/min. from 50 l/min. when a vertical lance was used. This condition gave only localised mixing in the torpedo, Fig. 44. It is known that some plants, mainly in Japan operate with vertical lances fitted with nozzles, using high injection velocities for the material. The model lance was fitted with a twin nozzle, and as a result the gas rate could be increased to 23 l/min., the nozzle tending to move the area of gas evolution within the torpedo, Fig. 45. The mixing produced covered the full length of the torpedo but left dead areas on the bottom corresponding to the junction of circulation zones.

METAL FLOW PATTERN DURING INJECTION

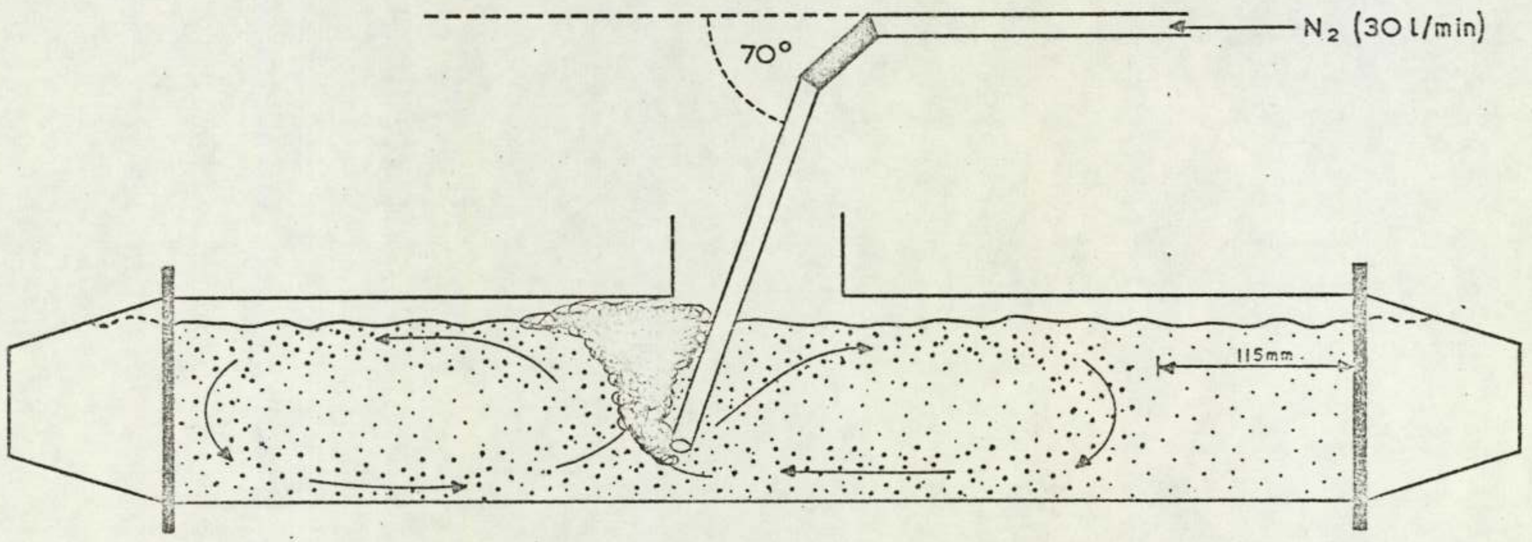


FIG 38

METAL FLOW PATTERN DURING INJECTION

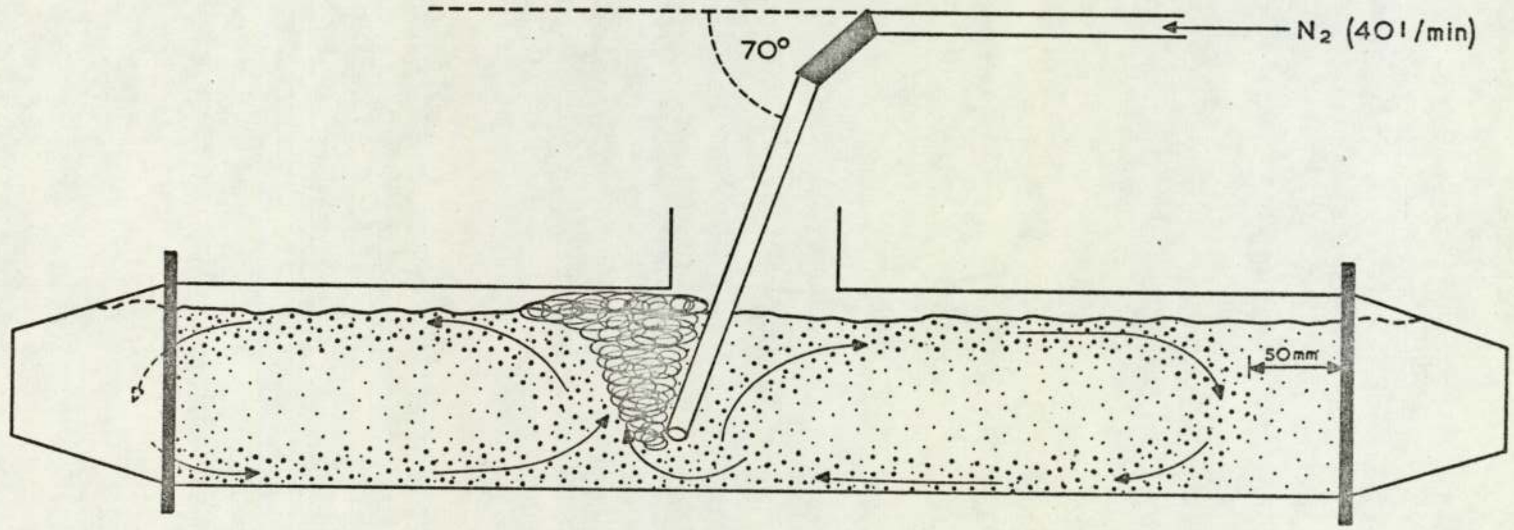


FIG 39

METAL FLOW PATTERN DURING INJECTION

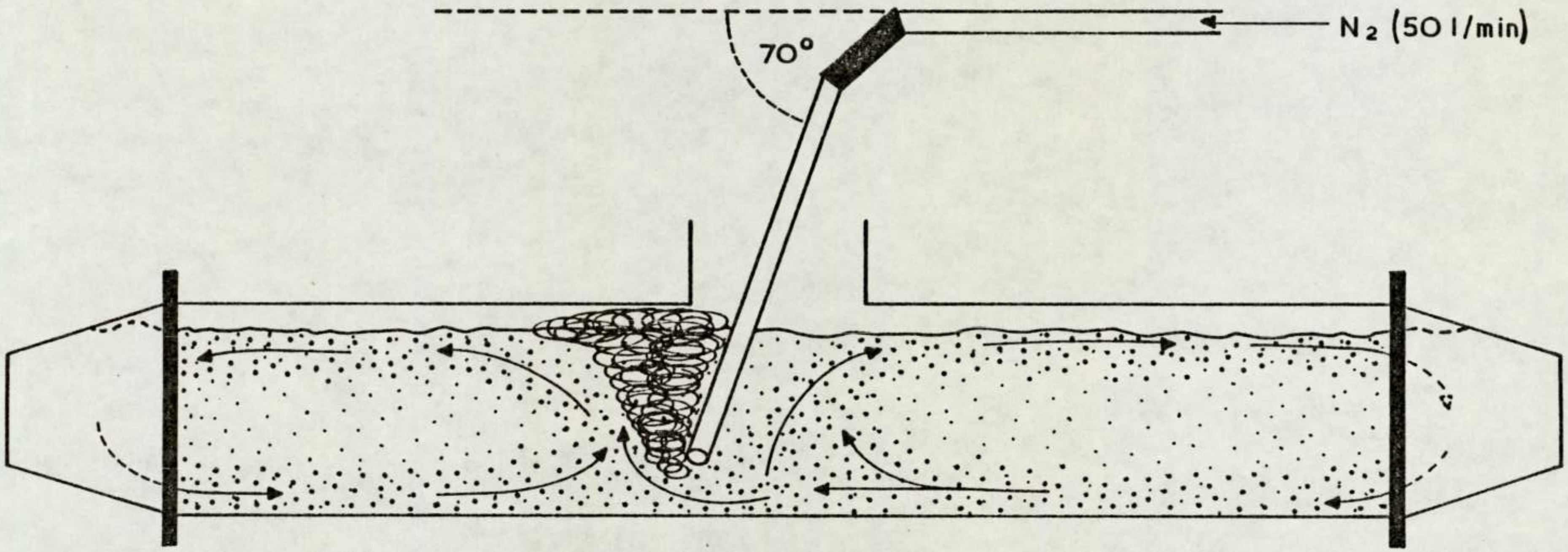


FIG 40

METAL FLOW PATTERN DURING INJECTION

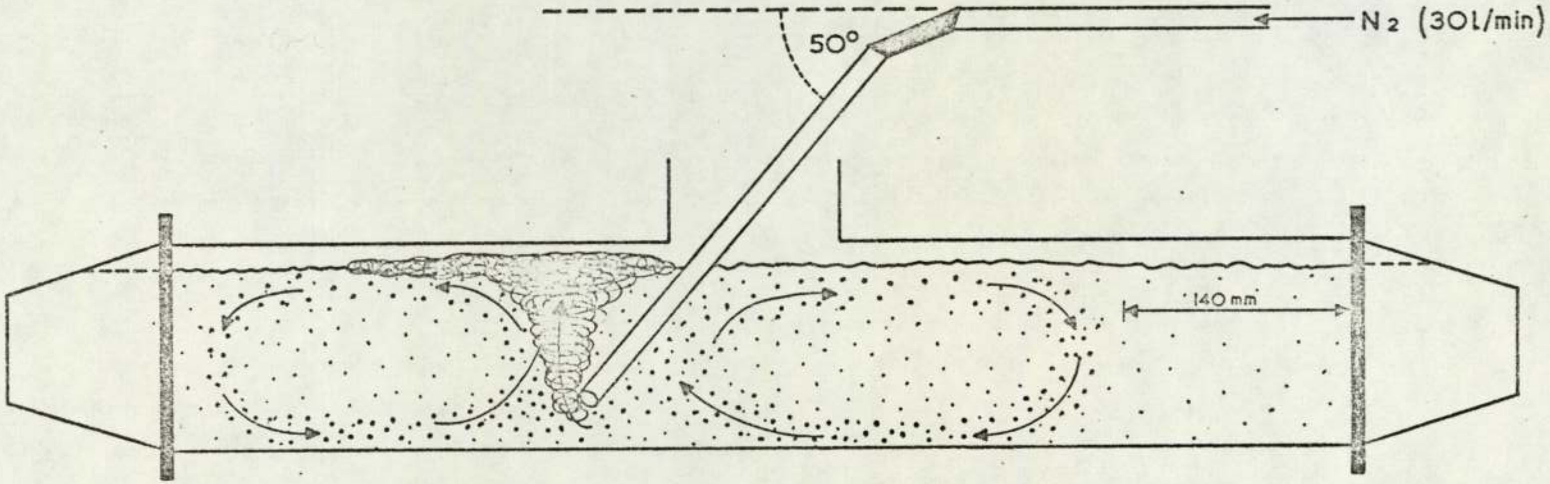


FIG 41

METAL FLOW PATTERN DURING INJECTION

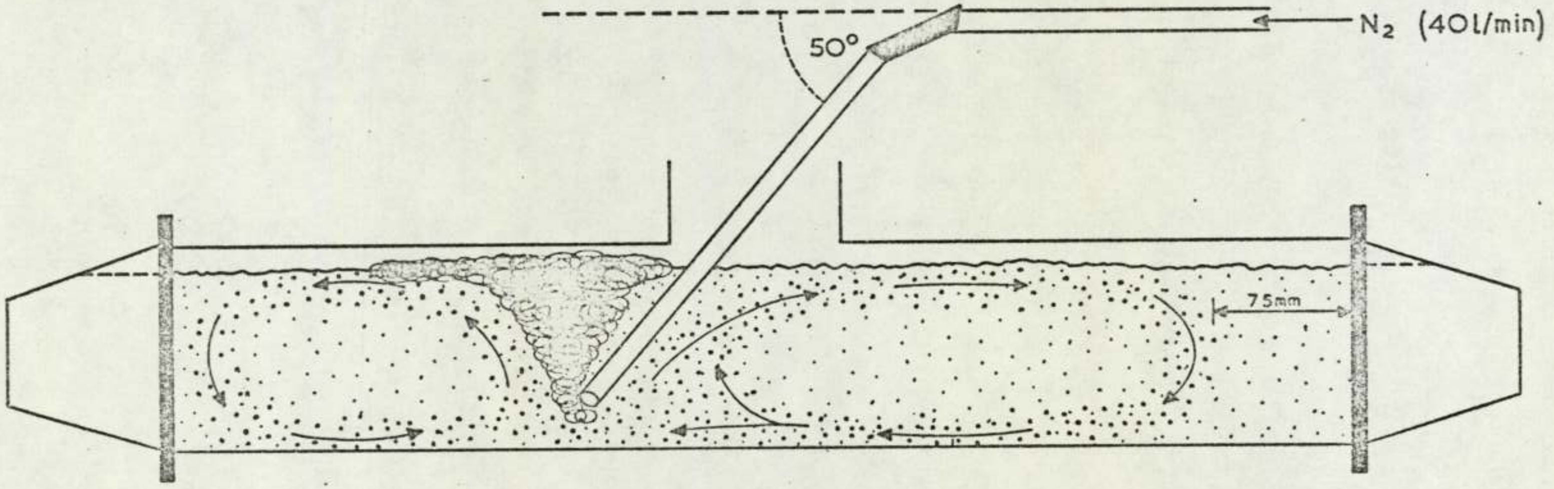


FIG 42

METAL FLOW PATTERN DURING INJECTION

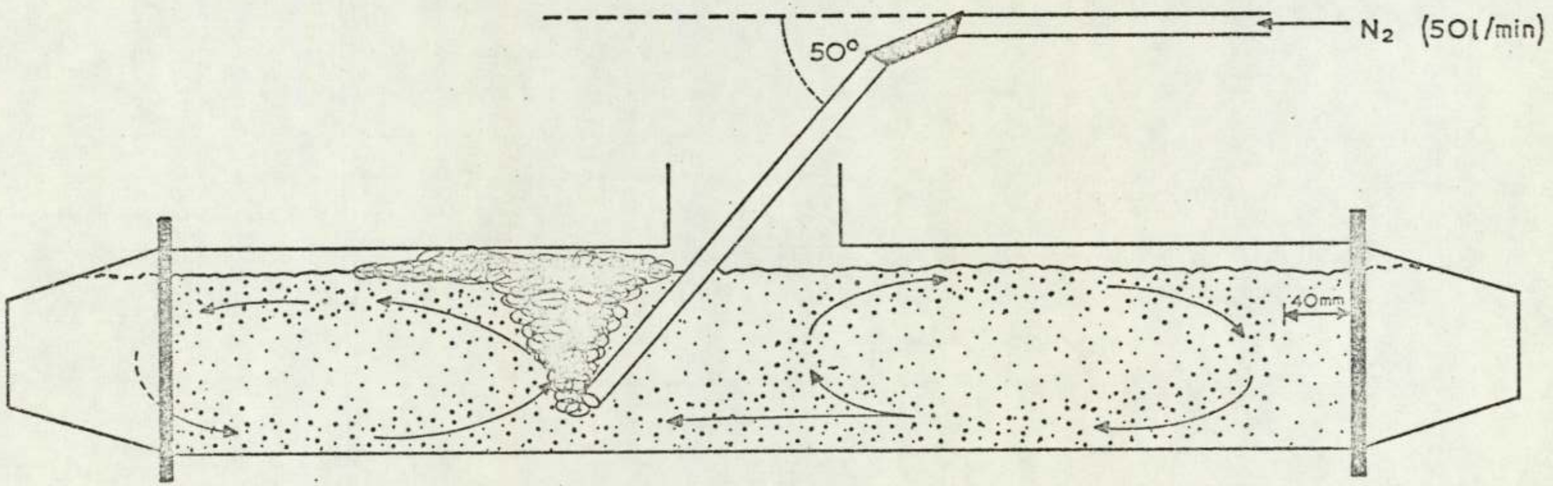


FIG 43

METAL FLOW PATTERN DURING INJECTION

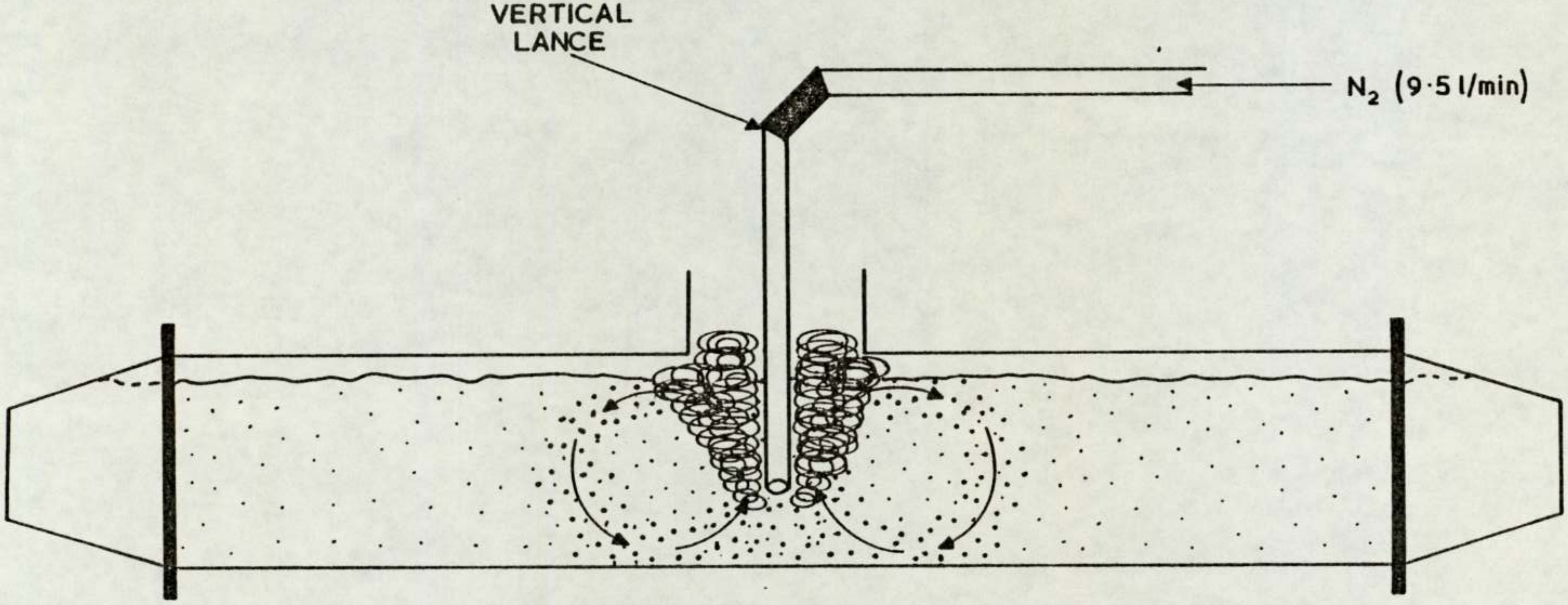


FIG 44

METAL FLOW PATTERN DURING INJECTION

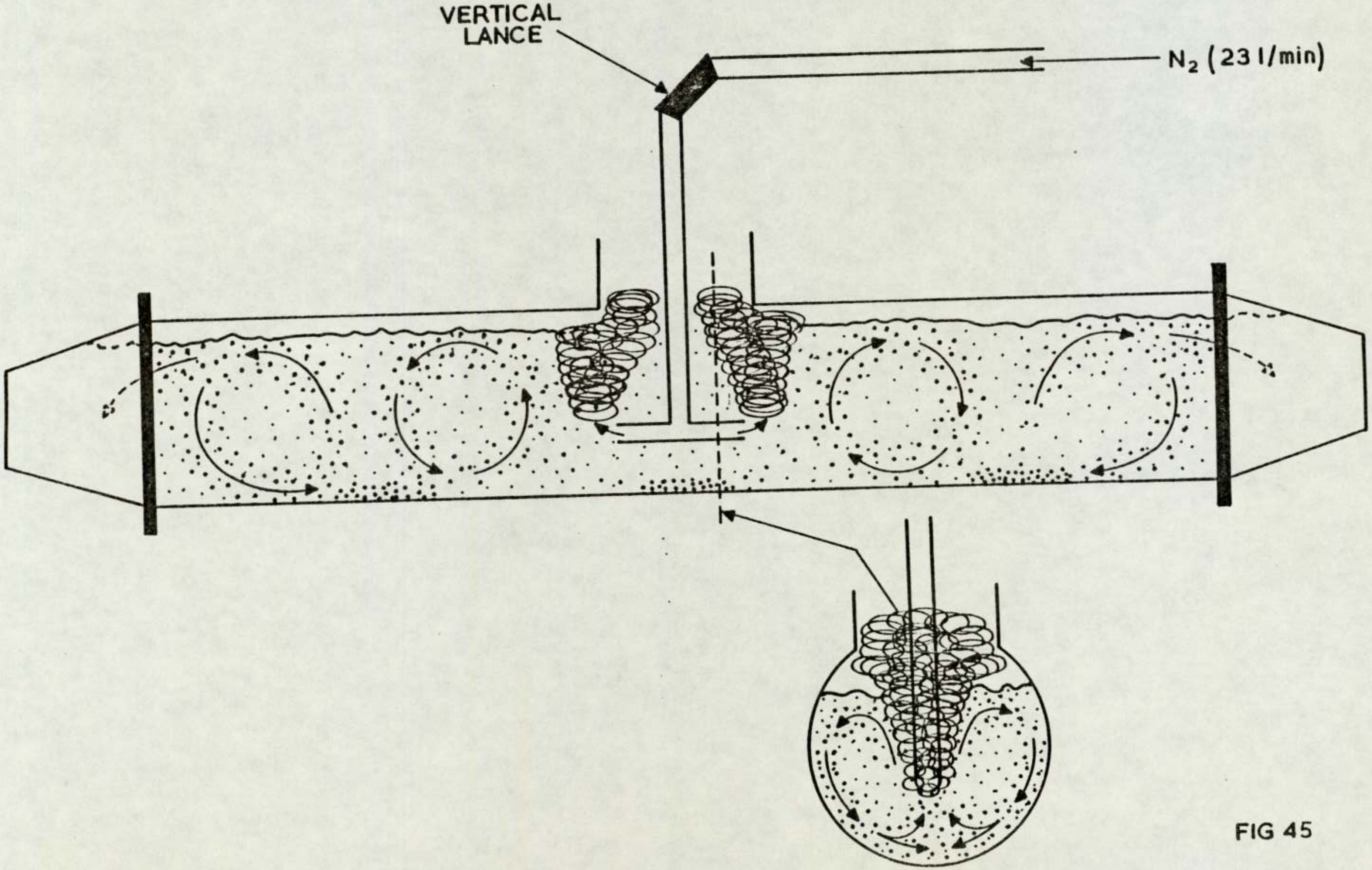


FIG 45

5.2.3. Discussion

In plant operation, splashing is a problem on very full torpedoes and is reduced by raising the lance and/or decreasing the material injection rate. Torpedo metal depths have been measured during trials by probing, and have tended to be below the nominal depth on which the model was based; depths ranging from 0.7 to 1.6 m. The resultant reduced lance immersion depths increase the compatibility of the plant and model gas rates, Table 15. It should be noted that in practice the torpedoes can contain significant bottom skulls of slag and metal, especially in the area below the torpedo mouth, and these seriously inhibit the plants ability to obtain maximum lance immersion. The results indicate that mixing of the total torpedo contents occurs under current plant operating conditions for an internally clean torpedo, but give no indication as to the rate of mixing.

If splashing were not a problem then a vertical lance would give the best mixing characteristics, i.e. a flow pattern covering the full length of the torpedo at a minimum gas rate. The experiments with a twin nozzle vertical lance show that if sufficient jetting could be produced from the nozzles, such that the gas evolution points were fully within the torpedo, this problem could be overcome. The efficiency of such a process would be dependent on ensuring that the correct gas velocities and powder distributions were maintained through the nozzles, and would require a tight specification on the material being used.

These reasons have promoted the use of the more flexible inclined lance systems throughout Europe and some are now being installed in Japan. However this is an area where further work using the model would be of interest.

The effect of overall gas rate as opposed to the calcium carbide content of the desulphurant has been illustrated in practice, Fig. 46. A significant plateau in consumption occurs as the carbide content is varied, the dominant factor being the stirring potential of the mixture.

5.3. Metal Mixing Times

5.3.1. Estimation of Time by Colour Change

5.3.1.1. Procedure

The model was set up with lance angles and gas rates as described in (4.4.2.). The time for homogenisation during injection was determined by the addition of $KMnO_4$ solution and noting the time for even colouration of the water. The dye was added as injection began, the experiment being repeated with dye added after 30 sec. injection.

5.3.1.2. Results

The results are given in Table 17. These data are fairly compatible within themselves, and are in line with the observations on homogenisation made previously. The most efficient mixing occurring at the larger lance angles and gas rates.

CONSUMPTION OF DESULPHURISING AGENT

(CALCIUM CARBIDE BASIS)

injection into 200t. capacity torpedo ladles

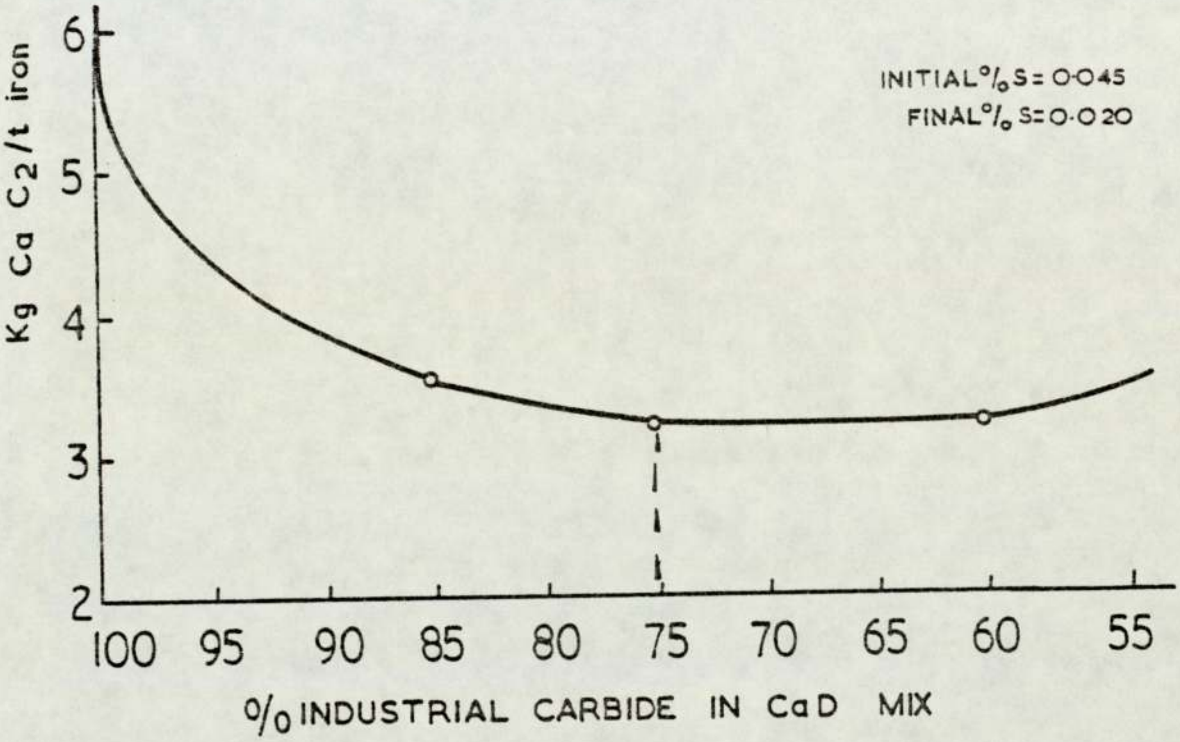


FIG 46

TABLE 17

RESULTS OF DYE EXPERIMENT ON TORPEDO MODEL

Lame Angle	Addition of 0.1n $KMnO_4$ Solution	Model Blow Rate (l/min)	Model Time (secs)	Calculated Plant Time (min)
70°	After 30 secs blowing	30	42.3	3.7
"	"	40	34.3	3.0
"	"	50	26.6	2.3
"	Prior to blowing	30	39.0	3.4
"	"	40	30.6	2.7
"	"	50	24.3	2.1
50°	After 30 secs blowing	30	54.3	4.7
"	"	40	45.0	3.9
"	"	50	35.3	3.1
"	Prior to blowing	30	54.6	4.8
"	"	40	47.6	4.2
"	"	50	39.3	3.4
Vertical	After 30 secs blowing	9.5	72.0	6.3
"	"	7.5		
"	"	5.0		
"	Prior to blowing	9.5	45.0	3.9
"	"	7.5		
"	"	5.0		
Vertical with twin nozzle	After 30 secs blowing	23.0	33.0	2.9
"	"	20.0	38.0	3.3
"	"	17.5	42.0	3.7

It was hoped that comparison of the results from the two dye addition methods would yield the time required for the circulation pattern to be established. However in this respect the data were inconsistent, and the time difference was small compared with the total time being estimated, Table 18. The maximum value obtained was 4 secs. corresponding to 21 secs. of real time, which is not significant in operating terms.

5.3.1.3. Discussion

The homogenisation time observed for the plant system of 70° and 50 l/min. is 26 secs. equivalent to 2.3 min. of real time. This is some 10% of the normal injection period and could be significant when trying to obtain an accurate post treatment sample.

Fixing the mixing time by the addition of a dye is prone to errors. The addition was made by both beaker and pipette with little difference between results obtained from the two methods. The major error is that in visually setting a time for even colouration.

5.3.2. Estimation of Time using a pH meter

5.3.2.1. Procedure

To obtain a more accurate and more comprehensive picture of the mixing mechanism the model torpedo was modified to take a pH meter probe at seven positions along its length. Three placements were made equidistant from each end and one between the lance exit and the torpedo centre line, Fig. 47.

TABLE 18

Time For Flow Pattern to Stabilise

Lance Angle°	Gas Rate l/min	Time to Stabilise* (sec)
70°	30	-3.33
	40	-3.67
	50	-2.33
50°	30	+0.33
	40	+2.66
	50	+4.00

* (Time, addn. after 30 sec. - Time, addn. prior to injection)

POSITIONS OF PROBE PLACINGS ON TORPEDO MODEL

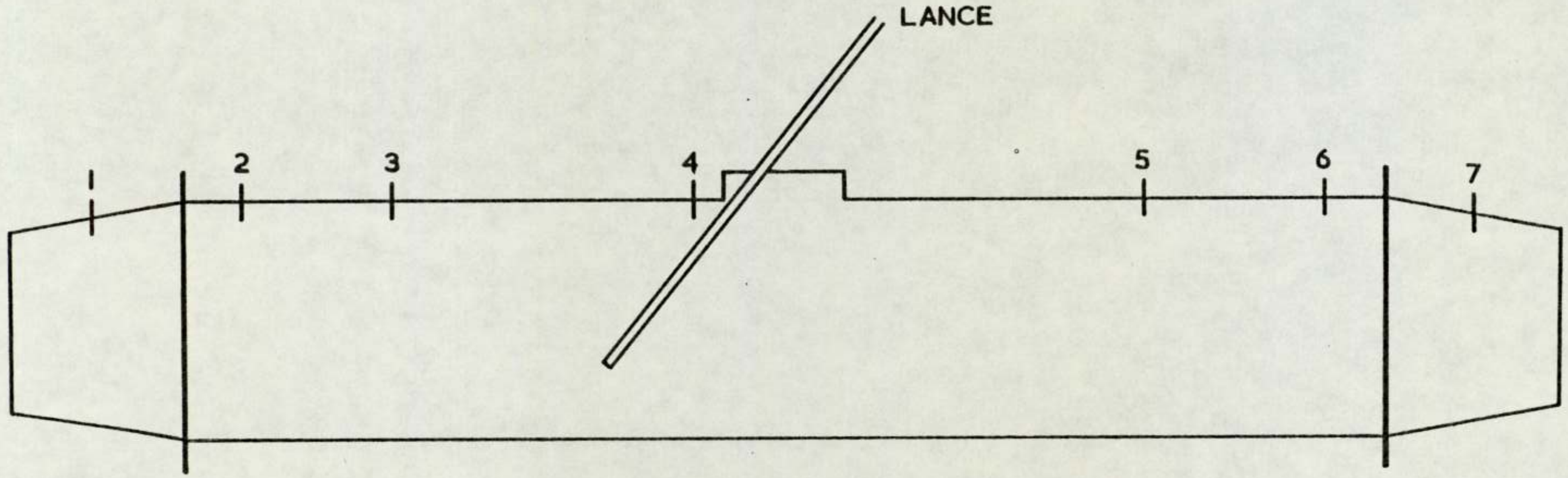


FIG 47

The output from the probe was passed through an amplifier to a single pen recorder. Each experiment was run by adding an equivalent volume of acid or alkali by beaker to the central position of the torpedo. The change in pH was noted on the recorder and the time to reach a plateau noted. Examples of the traces obtained are shown in Fig. 48. For each set of conditions and probe position the experiments were repeated three times or until reproducible traces were obtained.

1st time

5.3.2.2. Variation of Gas Rate

a) Results

It should be remembered that in this context gas rate refers to the overall rate of gas evolution from the process.

The results for a lance angle of 70° and varying gas flow rates are given in Fig. 49. As may be expected from the visual examination of flow patterns the minimum mixing time occurs just in front of the lance exit, and increases steadily as the distance from the lance increases. The averages of the mixing times for the overall torpedo length are given below.

TABLE 19

TORPEDO MODEL - AVERAGE HOMOGENISATION TIMES

Lance Angle	Model l/min.	Equivalent kg/min.	Homogenisation Time	
			model (sec.)	plant (min.)
70°	30	30	58.9	5.1
	40	40	45.1	3.9
	50	60	35.4	3.1

TYPICAL PH METER TRACES

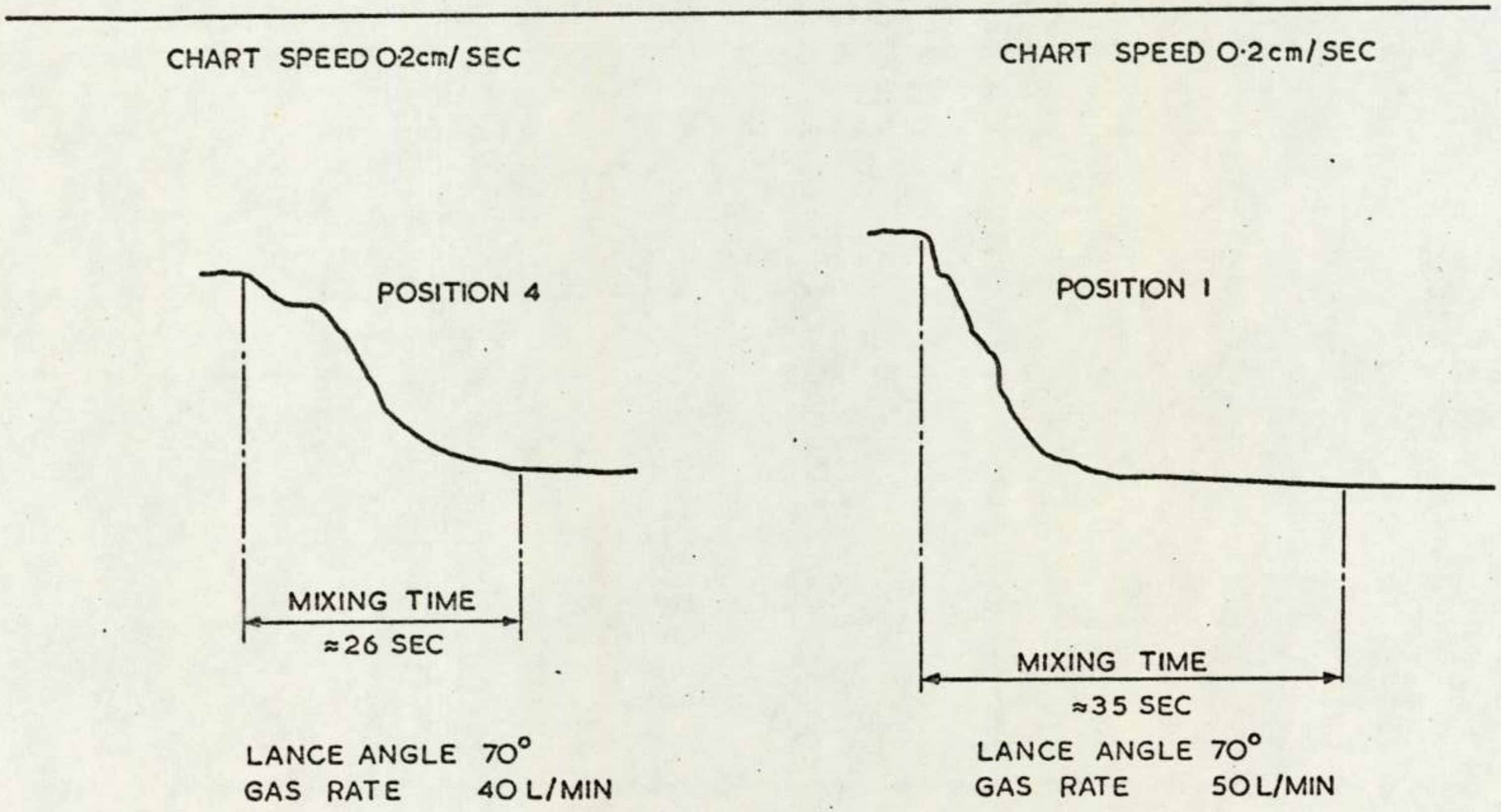


FIG 48

MODEL MIXING TIMES – GAS RATE VARIATION

LANCE ANGLE 70°
LANCE HEIGHT 2·5cm.

x = 30l/min
● = 40l/min
o = 50l/min

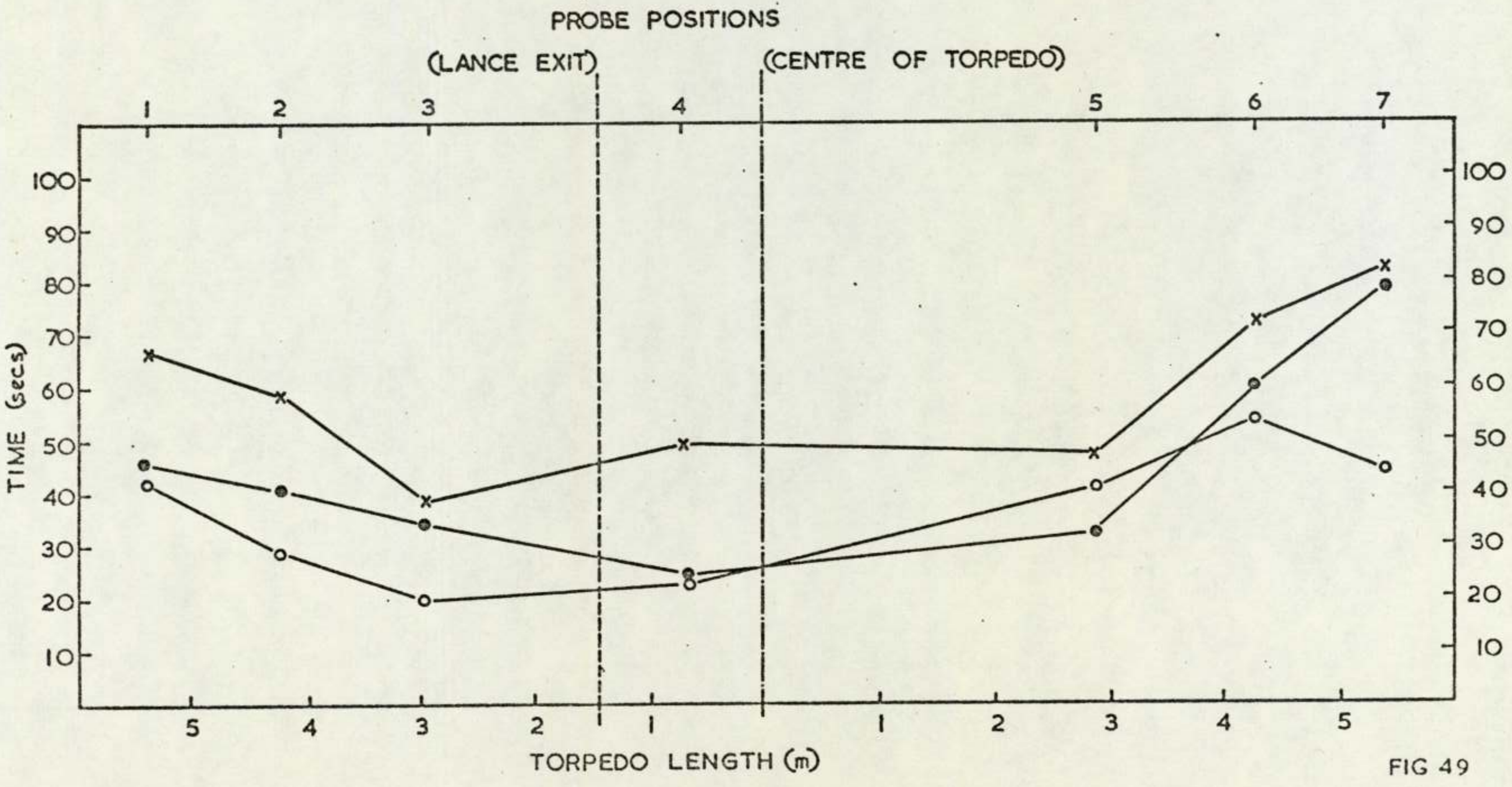


FIG 49

As the conical ends of the torpedo are approached the time increases more rapidly especially at the end furthest from the lance. The mixing time for this zone is probably a better indicator of process efficiency.

TABLE 20

TORPEDO MODEL END ZONE HOMOGENISATION TIMES

Lance Angle	Model l/min.	Equivalent kg/min.	Homogenisation Time*	
			model (sec.)	plant (min.)
70^o	30	30	77	7.6
	40	40	69	6.0
	50	60	48	4.2

* Mean time for probe positions 6 & 7

b) Discussion

The data suggest that in the body of the torpedo there is little benefit to be obtained by increasing the mixing potential of the process above that already used, in fact slightly lower levels could be tolerated. Too low a level, obtained either by reducing the material rate or lowering the proportion of carbonate in the mixture, rapidly reduces the mixing efficiency. The rate of 30 l/min. in the model corresponds to approximately 30 kg/min. of CaD in practice and at the centre of the torpedo increases the homogenisation times to 49 secs. from 22 and 24 secs. at 50 and 40 l/min. respectively. In relation to the plant that is 4.3 min. for mixing, an increase of 2.3 min. At the end of the torpedo away from the lance this difference is increased to 3.4 min.

The effect of the higher gas quantities is more marked at the ends of the torpedo. The mixing energy is obtained from the rising gas bubbles, and its effects should therefore be equal equidistant from the lance exit. This is not the case, the end effects produced in the torpedo cone nearest the lance increase the homogenisation time in that area. Some of the energy input is therefore wasted by not having a central lance exit. At the opposite end of the torpedo the times increase still further as the distance from the lance increases. This was shown as a potential dead zone when flow patterns were examined.

5.3.2.3. Variation of Lance Angle

a) Results

The results for lance angles of 50°, 60° and 70° are given in Fig. 50. The pattern already established for mixing times is reproduced, showing maxima at the torpedo ends. Averages of the mixing times for the whole torpedo length are given below.

TABLE 21

TORPEDO MODEL AVERAGE HOMOGENISATION TIMES - VARIABLE LANCE ANGLE

Lance Angle	Model l/min.	Homogenisation Time	
		model (sec.)	plant (min.)
70	40	45.1	3.9
60	40	46.9	4.1
50	40	50.4	4.4

MODEL MIXING TIMES – LANCE ANGLE VARIATIONS

LANCE HEIGHT 2·5cm.
GAS FLOW RATE 40 l/min

LANCE ANGLE o = 50°
x = 60°
● = 70°

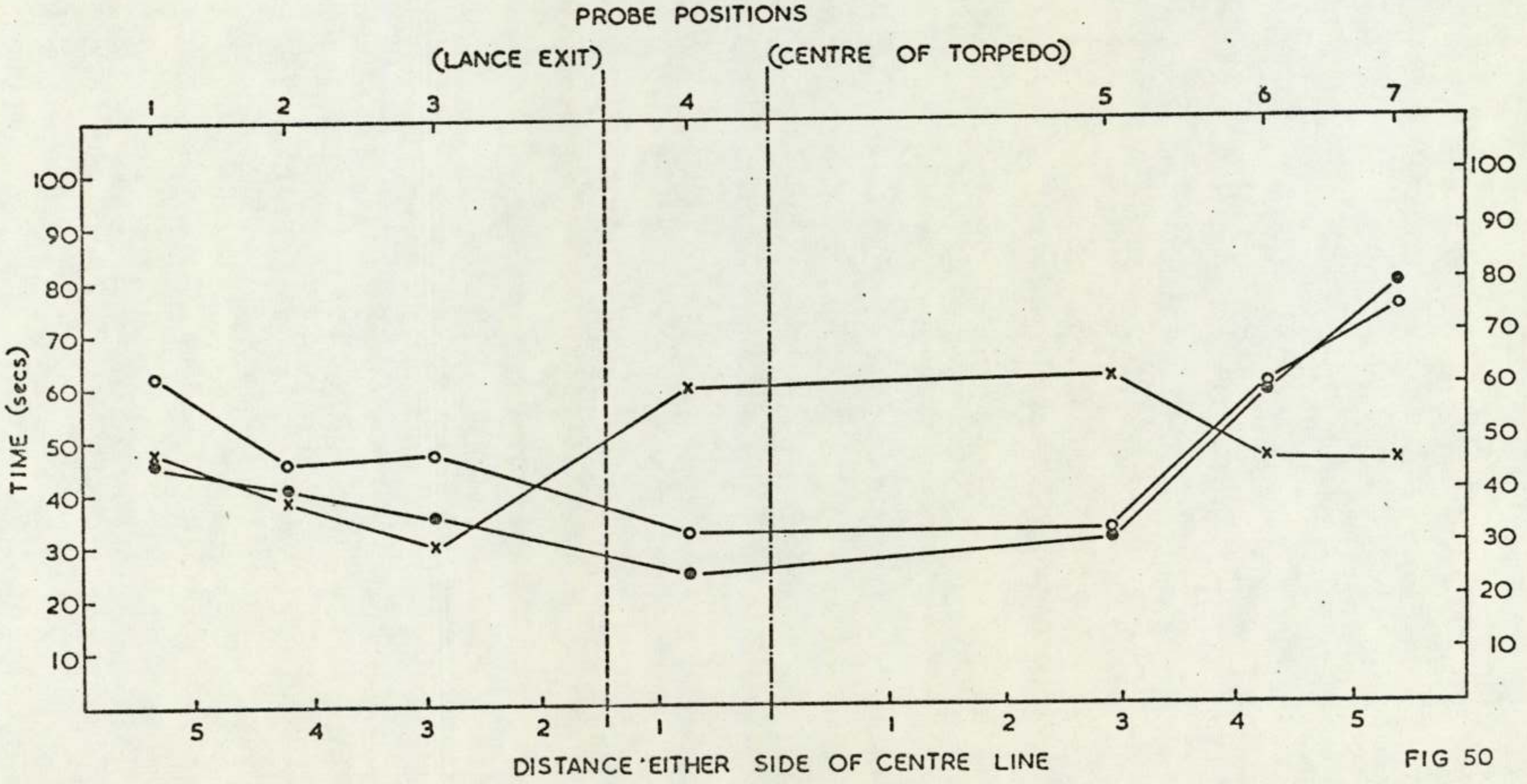


FIG 50

At the torpedo end nearest the lance exit the times increase as the lance angle is reduced, agreeing with the visual estimations. A minimum is produced near the torpedo centre. Along the torpedo away from the lance the mixing times for 70° and 50° are almost identical.

TABLE 22

TORPEDO MODEL HOMOGENISATION TIMES - END ZONES

Lance Angle	Model l/min.	Mean Homogenisation Time-Model (sec.)	
		Probe Position 1 and 2	Probe Position 6 and 7
70	40	43	69
60	40	43	46
50	40.	54	68

b) Discussion

The conclusion of the previous work (sect. 5.2.) that a 70° lance angle is to be preferred is confirmed. The results indicate that at the gas flow rate used reductions in lance angle do not significantly effect mixing at the torpedo end away from the lance. The distance from the lance is so great that similar results are produced.

The data recorded for a 60° angle do not fit the general pattern of results. There is no obvious explanation for this. It was thought that if the injected gas was imparting a significant quantity of kinetic energy to the water then the swirling motion produced could give the results noted. However this was not corroborated by the results for the 50° lance angle.

5.3.2.4. Variation of Lance Immersion Depth

In all the experiments the immersion depth of the lance was kept constant at 25 mm. above the base of the torpedo. In practice this situation is rare, because of variations in the metal weight carried and the build up of a skull in the torpedo. To illustrate the effect of reduced immersion on mixing time the model was set up with the lance at 50 mm. from the base equivalent to 300 mm. on the plant.

a) Results

The results are shown in Fig. 51, for comparison with Fig. 49. At the torpedo end nearest the lance the mixing times were significantly increased by the reduced immersion depth, the change averaging 31.3 secs. for probe positions 1, 2 and 3, at the plant equivalent gas rate of 50 l/min. This is equivalent to 2.7 min. of plant time. Away from the lance as the distance from the lance exit increases the effect of immersion becomes less significant and the times recorded merge with previous results. The overall homogenisation time increasing by only 10 secs.

b) Discussion

The increase in time measured for probe positions 1, 2 and 3 represents a doubling in the mixing time for 25% of the torpedo contents. If other factors could be ignored this would have a direct effect in reducing the efficiency of desulphurisation on plant.

MODEL MIXING TIMES - DECREASED LANCE IMMERSION

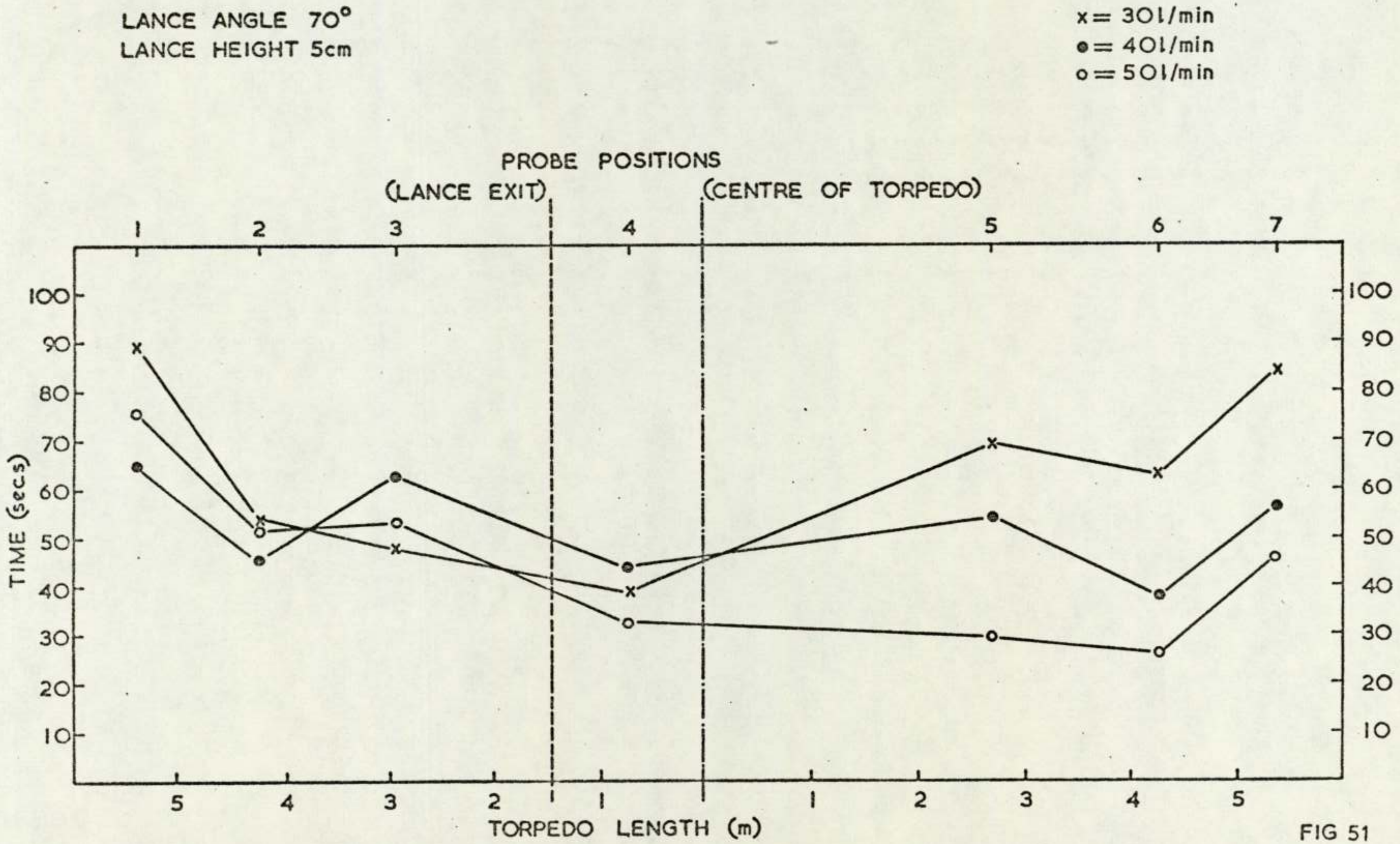


FIG 51

Evidence of this effect is being collected and will be reported in the extension of this work.

When attempting to relate plant results to possible differences identified by modelling the relative lance immersion depths require careful scrutiny. The influence of plant lance immersion on model gas rate is shown in Fig. 52.

5.4. The Influence of Torpedo Skulls

A common problem when torpedo ladles are used for the transport of iron is the increase in tare weight of the ladle which reduces the iron carrying capacity. Under normal operation, for iron transport only, the problem can be controlled by optimising transfer times between filling and emptying, and by frequent draining of residual metal and blast furnace slag. However when the torpedo is used as the reaction vessel for a calcium based desulphurisation process the character of the problem changes. Blast furnace slag is relatively silica rich and fairly fluid, but when this is mixed with the lime product of desulphurisation the slag becomes very viscous and is probably only completely molten at temperatures over 2000^{o}C. Desulphurisation slag which is not mixed in this way takes the form of spheres, about 10 mm. diameter. When cold, this slag falls to a powder, but when hot it forms a strong solid mass as the spheres frit together.

THEORETICAL GAS RATES VS LANCE IMMERSION DEPTH

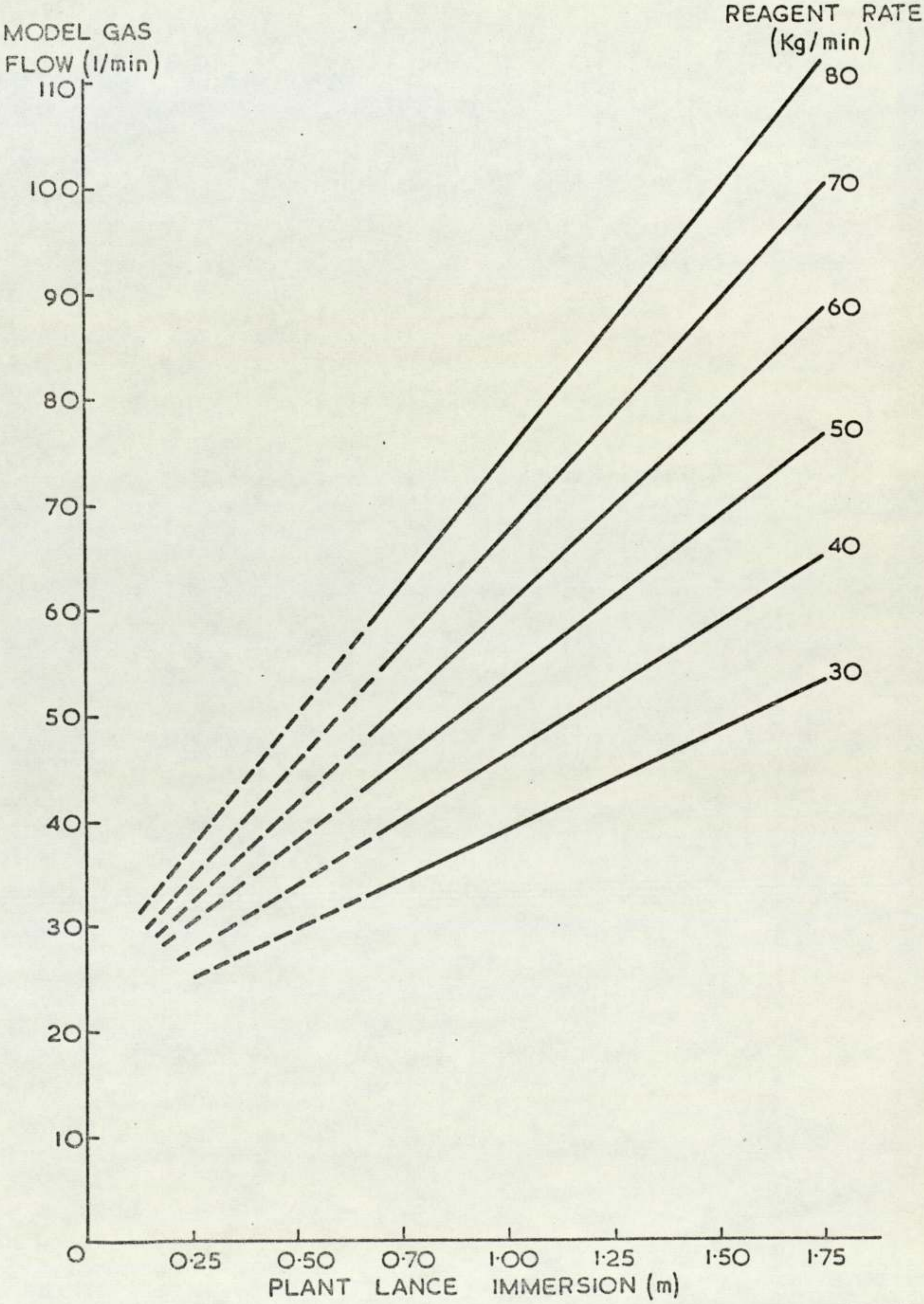


FIG. 52

These desulphurisation slags are difficult to remove from the torpedo using the normal draining, or pouring techniques, and as a result form a recirculating slag load. This has two effects, 1) when settled in a torpedo the slag forms a permanent skull; 2) during desulphurisation the residual slag is impacted directly by the desulphurising agent and causes a build up beneath the lance.

The shape of the skull was determined by the internal examination of a number of torpedoes as they were taken out of service. The skull was simulated by plasticene and the model run at a 70° lance angle and varying gas rates, using polystyrene beads to examine the flow patterns produced.

a) Results

The flow patterns obtained are illustrated in Figs. 53-55. The principal effect of the skull was to centralise the mixing force around the lance exit. At the high flow rate, 50 l/min. a dead zone with no mixing was produced at the end away from the lance, where none existed without the skull. At the lower gas rates dead zones were produced at both ends of the torpedo. The size of the zone increased as the gas rate reduced.

INFLUENCE OF TORPEDO SKULL ON MODEL FLOW PATTERN

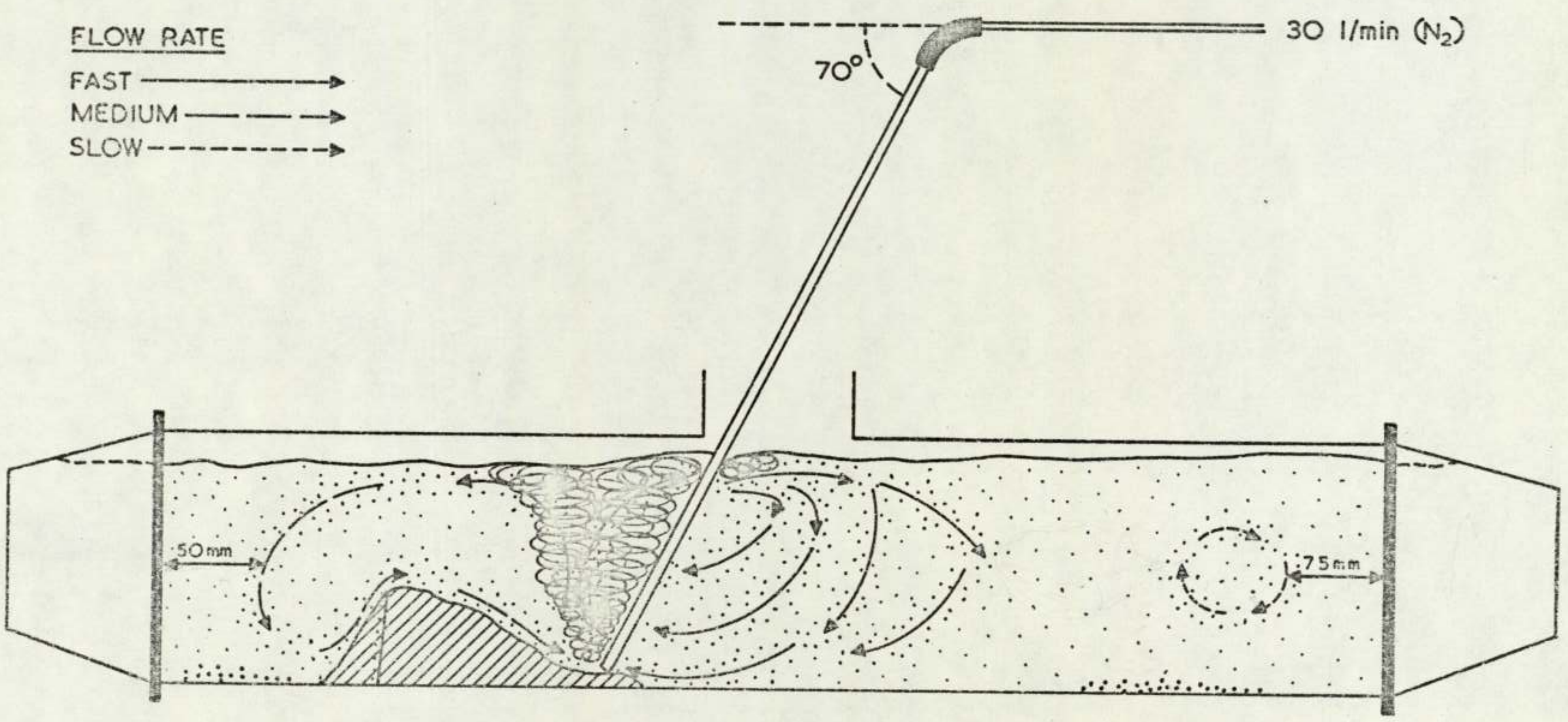


FIG 53

INFLUENCE OF TORPEDO SKULL ON MODEL FLOW PATTERN

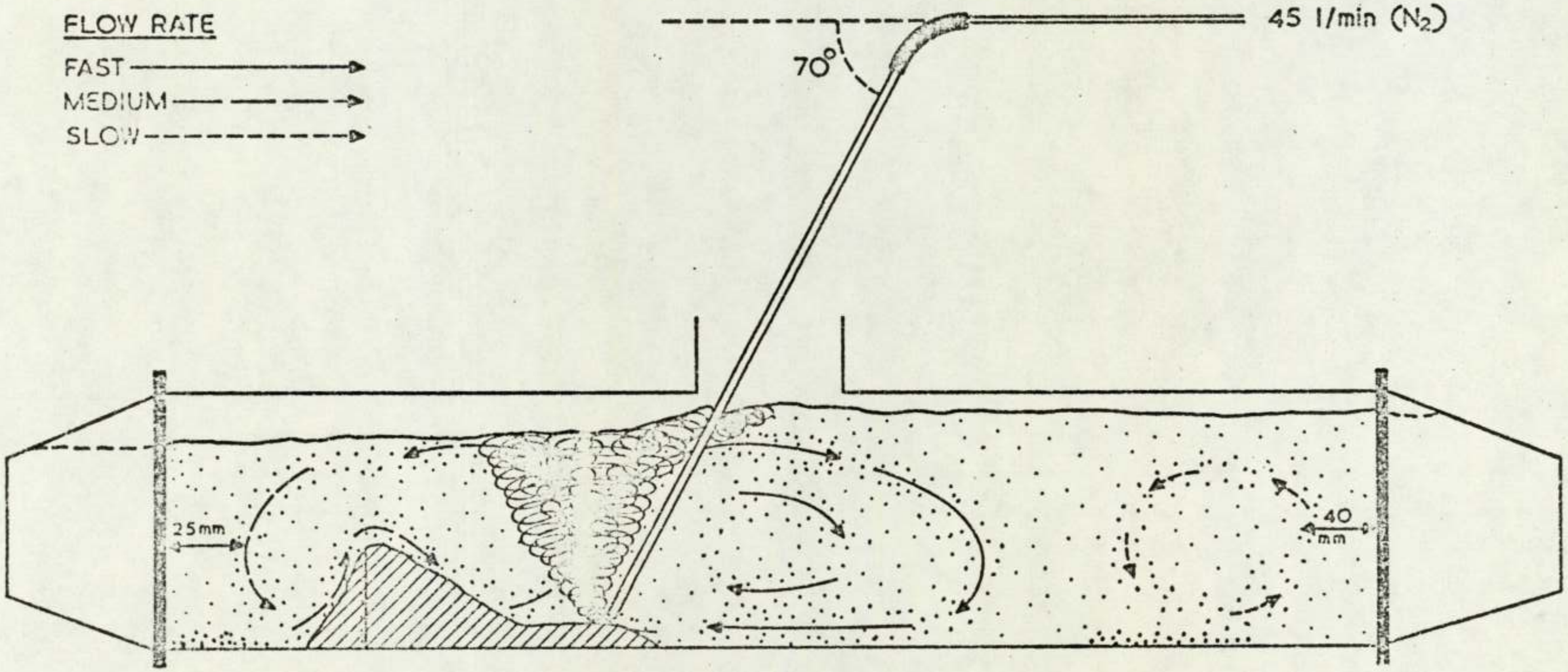


FIG 54

INFLUENCE OF TORPEDO SKULL ON MODEL FLOW PATTERN

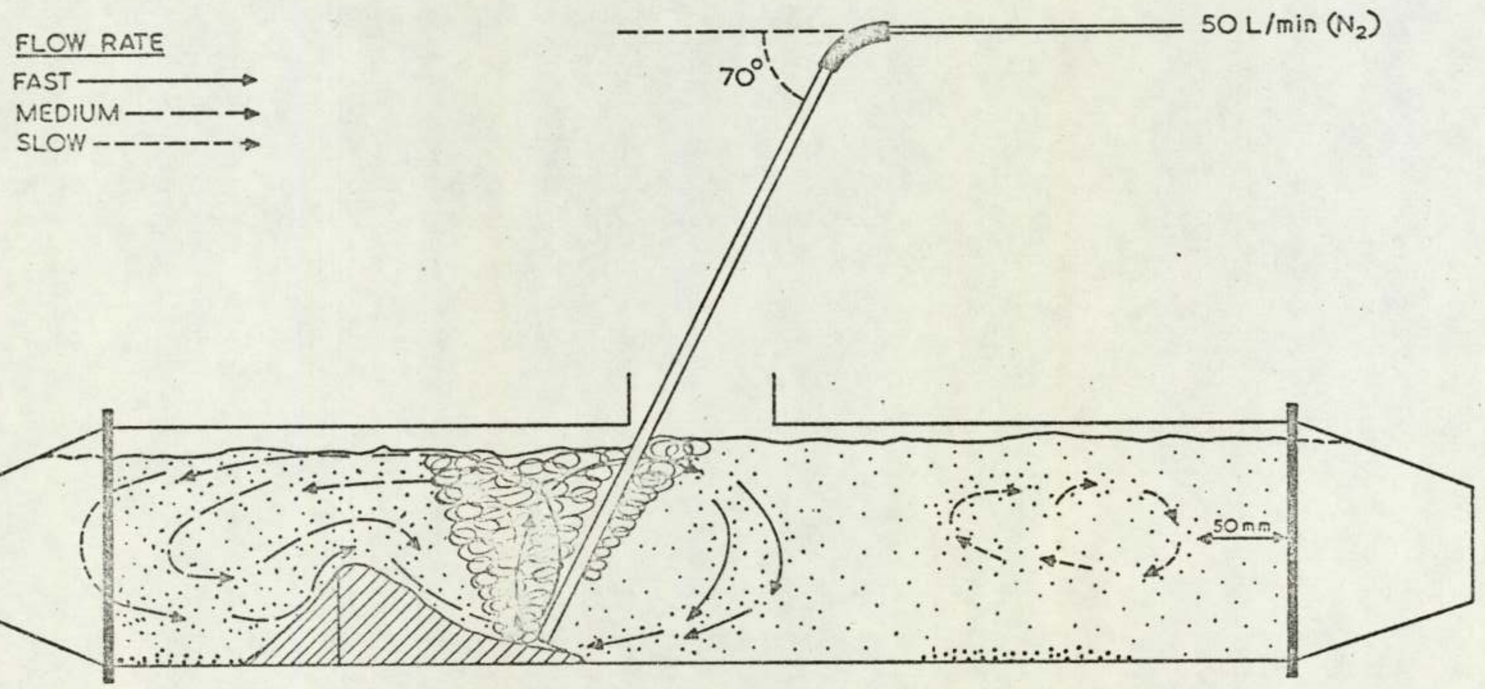


FIG 55

TABLE 23

TORPEDO MODEL EFFECT OF SKULL ON DEAD ZONE LENGTH

Model Gas Rate l/min.	Plant Equivalent kg/min.	Length of Dead Zone			
		End Near Lane		End Away from Lance	
		Model (mm)	Equivalent Plant (m)	Model (mm)	Equivalent Plant (m)
50	60	0	0	67	0.8
45	50	41	0.5	54	0.6
30	30	67	0.8	92	1.1

b) Discussion

The possible effect of a skull of the type modelled on desulphurisation performance is self evident. In the model studies the lance immersion was maintained at the previously used value. In practice however the skull is often positioned so as to prevent the lance reaching the normal blowing position. The lance has to be raised some distance above the skull to prevent blockage, and this in turn further reduces lance immersion and treatment efficiency deteriorates. Examination of the structure of the skulls showed them to be constructed of layers of iron and a carbide derived slag. This suggested that if the lance remains too close to the skull during injection, direct adhesion occurs and the rate of skull build up is increased. At this time no recommendations can be made on preferred injection practices to minimise skull effects and build up.

The model studies considered a single skull only. In practice smaller skulls occur on the opposite side of the torpedo mouth to the one used,at each end, and to some degree around the whole torpedo diameter. The results observed therefore state a minimum effect rather than a mean or maximum.

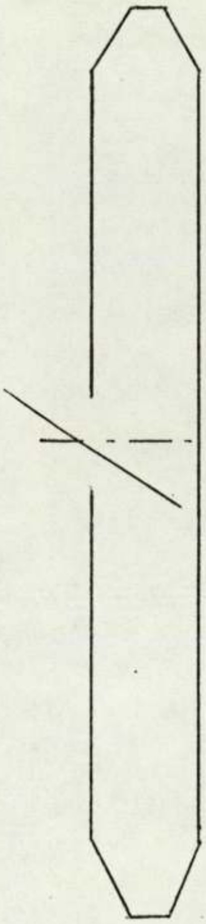
Plant trials on this subject and means of combating skull formation will be considered in sections 7 and 8.

5.5. Veracity of Post-Treatment Sample

In addition to enabling the comparison with other operating conditions the model data for the assumed plant situation gives an indication of how representative the post-treatment sample is with respect to the mean metal analysis, Table 24. This is of particular importance when attempting the production of very low sulphur steels and in the calculation of process efficiency. The results show a difference of approximately 2 min. between homogenisation times for the centre and ends of the torpedo. During treatment the rate of sulphur removal is highest at high concentrations. If injection ceases when the removal rate is high the difference in analysis between the centre and the ends will be at a maximum. On the Appleby-Frodingham Works plant the final sulphur is in the range 0.005% - 0.020%. At this level the rate of reaction is relatively low, hence minimising the sampling and reagent optimisation error/efficiency calculation error. This would of course be strongly influenced by the presence of skulls, inadequate lance immersion or low reagent delivery rate.

TABLE 24

Model and Plant Estimated Metal Homogenisation at 70° Lance Angle and 50 l/min Gas Rate



Distance Along Torpedo m.	Homogenisation	
	Model Time (Sec)	Plant Time (min)
5	46	4.02
4	51	4.45
3	41	3.58
2	36	3.14
1	31	2.71
0	26	2.27
1	22	1.92
2	21	1.83
3	20	1.75
4	27	2.36
5	37	3.23

6. PLANT USE OF TORPEDO MODEL RESULTS

6.1. Adjustments to Plant Operation

In operating a torpedo injection plant the two plant factors which control reagent consumption are the initial sulphur level and the level to which the torpedo is filled.

The desulphurisation efficiency (Appendix 1) of the process is known to increase as the reagent addition rate is reduced. As the latter is reduced the rate of supply of CaC_2 falls, but, as the model work has shown, the stirring energy imparted to the iron is still high. The result is a better utilisation of the CaC_2 with respect to its reaction with sulphur. The model indicated that a threshhold value would be reached below which the effective mixing of the iron would be reduced. This lower level was 50 kg/min.

A study of plant data, examining the effects of both metal weight treated (equivalent to metal depth) and initial sulphur level indicated that the major reduction in efficiency began at less than 0.055%S and 160 t. of metal.

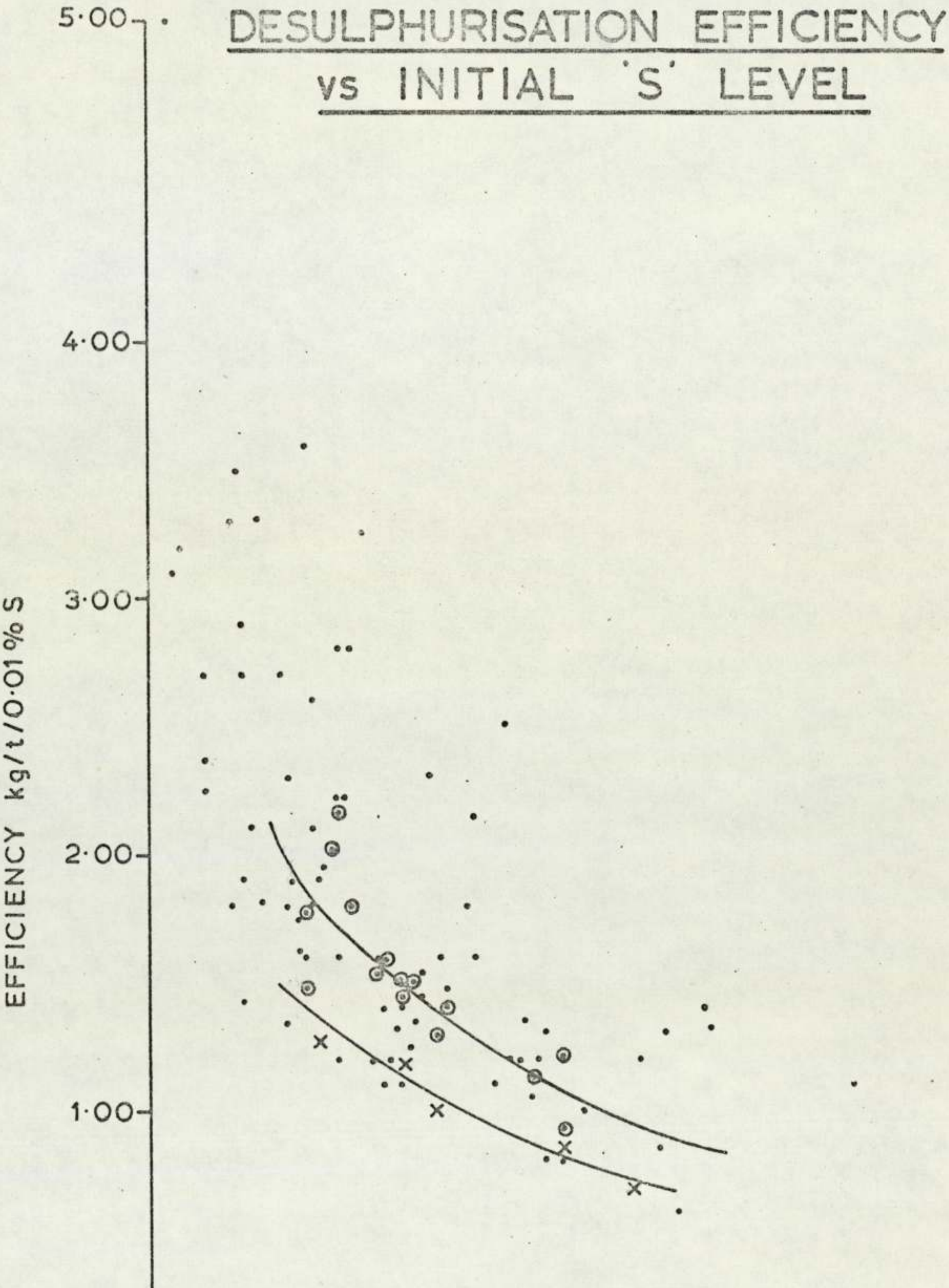
The graph, Fig. 56, representing all the good quality data from a normal four week operating period, identifies those torpedoes treated for steel to be continuously cast and those for ingot route steel, i.e. final iron sulphur levels of 0.010% and 0.020% respectively, for iron weights greater than 160 t.

It is evident that at the high weights and sulphur levels plant desulphurising performance is more predictable than when these conditions are not met.

This point is further emphasised by the plant data in Table 25. Routine data is analysed in two groups, defined by end use either concast or ingot route. Plant scheduling defines the initial sulphur levels for each group to optimise the iron desulphurisation - steelmaking process as a whole in terms of torpedo skulling and B.O.S. iron charging ladle slag sulphur content. Further categorisation of the data is not done. When the torpedo treatments with low weight and sulphur level are separated from the routine data there is a significant improvement in the efficiency factor value. For the casts below the recommended limits, in the units of the Table, efficiency is reduced by 0.083 and 0.032 (kg CaD/t. metal/0.001%S removed) for concast and ingot route treatments respectively. Data of this type from a control trial on the plant have been costed, Fig. 57. Taking 240 t. as the maximum weight which could be treated, a reduction to 140 t., as an average, costs an extra £300,000 per year (1978 costs) in terms of desulphurising agent alone.

Although the previous model work had been applied to high metal weights it was concluded, following discussions with plant management, that the reduced injection rate could be applied to each of the above conditions. The operation of the plant was therefore modified so that injection rates of 50 - 60 kg/min. were used on the low metal weight and/or low sulphur torpedoes.

A second aspect of this work, following discussions with the Process Mathematics Section at Scunthorpe Works was the recommendation of an improved monitoring system for plant performance. The practice had been to record the treatment conditions for every torpedo and from these data calculate an average carbide efficiency. Although useful in overall terms, this did not reflect the actual performance of the plant since it neglected the effect of variable metal weight. It was therefore recommended that the efficiency factor should also be calculated and reported for those treatments where the metal weight was greater than 180 t. This figure was set tc give a good safety margin over the 160 t. previously used.



◎ CONCAST × ORDINARY

FOR METAL WT. >160t

FIG. 5

TABLE 25

Effect of Low Metal Weight and Initial Sulphur Level on Performance

	CONCAST Efficiency kg/t./.001% S_R			ORDINARY Efficiency kg/t./.001% S_R		
W./E.	Routine Reported Data	Routine Excluding HM $\leqslant$ 165t $\%S_I \leqslant .055$	HM $\leqslant$ 165 $\%S_I \leqslant .055$ ONLY	Routine Reported Data	Routine Excluding HM $\leqslant$ 165t $\%S_I \leqslant .055$	HM $\leqslant$ 165t $\%S_I \leqslant .055$ ONLY
27/11/77	.156	.134	.236	.098	.094	.112
4/12/77	.150	.135	.194	.116	.110	.194
11/12	.158	.126	.203	.107	.102	.115
18/12	.148	.129	.224	.111	.107	.130
25/12	.135	.124	.193	.120	.109	.182
1/1/78	-	-	-	-	-	-
8/1	.154	.126	.231	.108	.106	.118
15/1	.139	.119	.193	.115	.115	.118
Average	.149	.128	.211	.111	.106	.138

EFFECT OF METAL WEIGHT ON DESULPHURISING AGENT CONSUMPTION AND COST

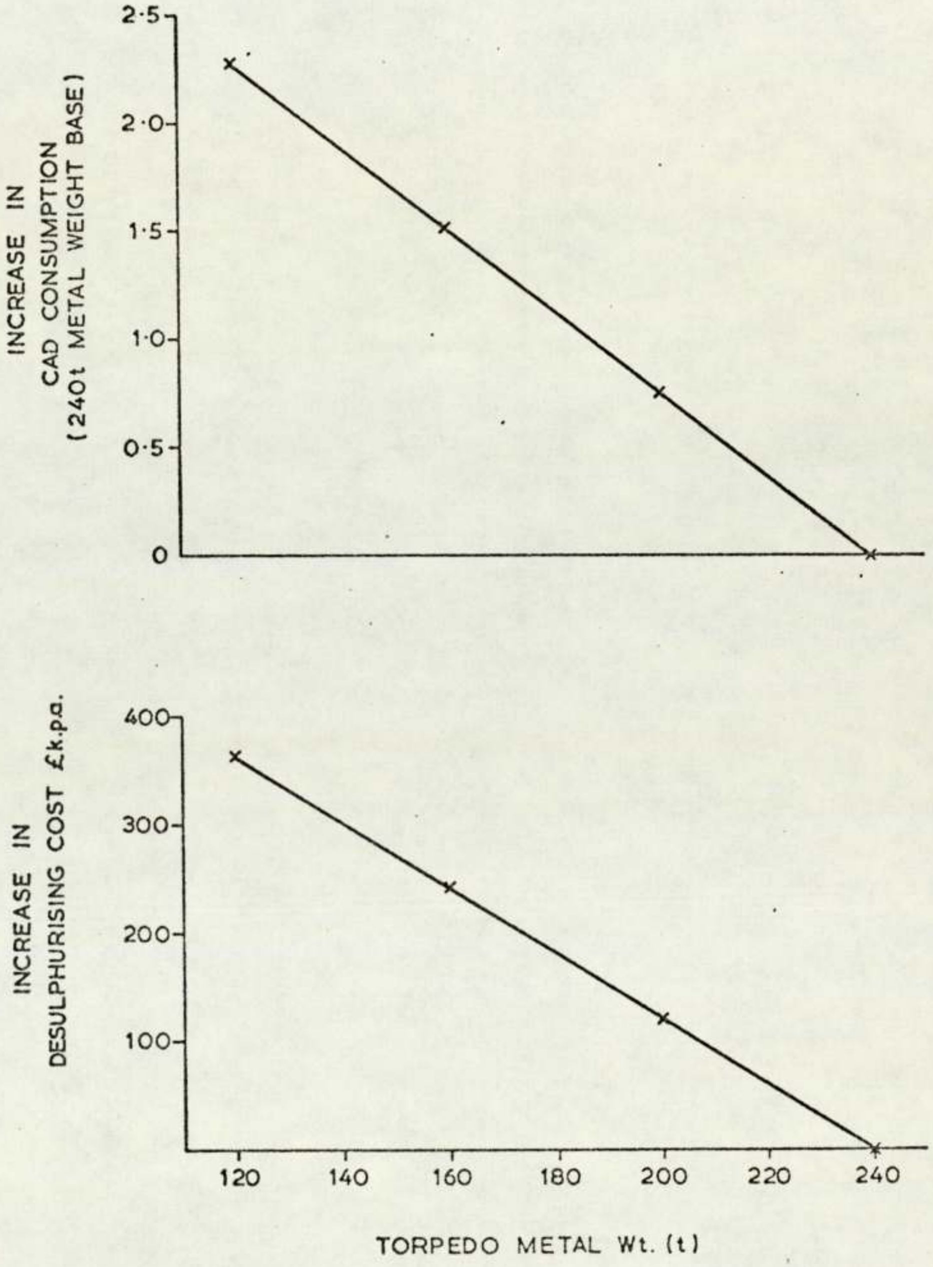


FIG. 57

7. TORPEDO MOUTH DESIGN

7.1. Introduction

One of the problems of the torpedo desulphurisation process, as has been discussed, is the recirculating slag load, which with attendant skulls causes a reduction in desulphurising efficiency. After the metal had been poured the ladle's shape made it difficult, even with good draining facilities, to remove the slag. The Appleby-Frodingham B.O.S. plant has skimming machines for the removal of slag from the iron transfer ladles,so that any slag carried over from the torpedoes can be prevented from entering the B.O.S. vessel. However, the torpedo mouth design was such that the large rafts of slag formed during desulphurisation often blocked the mouth and acted as weirs - retaining the slag which otherwise would have flowed through. It was also noted that fast pouring rates tended to bring more slag from the torpedo. To examine the effects of mouth design and pouring rate on slag removal a number of model experiments were made.

7.2. Torpedo Model Experiments and Results

A torpedo model, identical to that used for the metal mixing experiments, was constructed but with an exchangeable centre section. Three pouring mouth designs were used, Fig. 58.

a) Rectangular.

b) 50 mm. radius (equivalent to normal plant configuration).

c) 40 mm. radius.

TORPEDO MOUTH DESIGNS

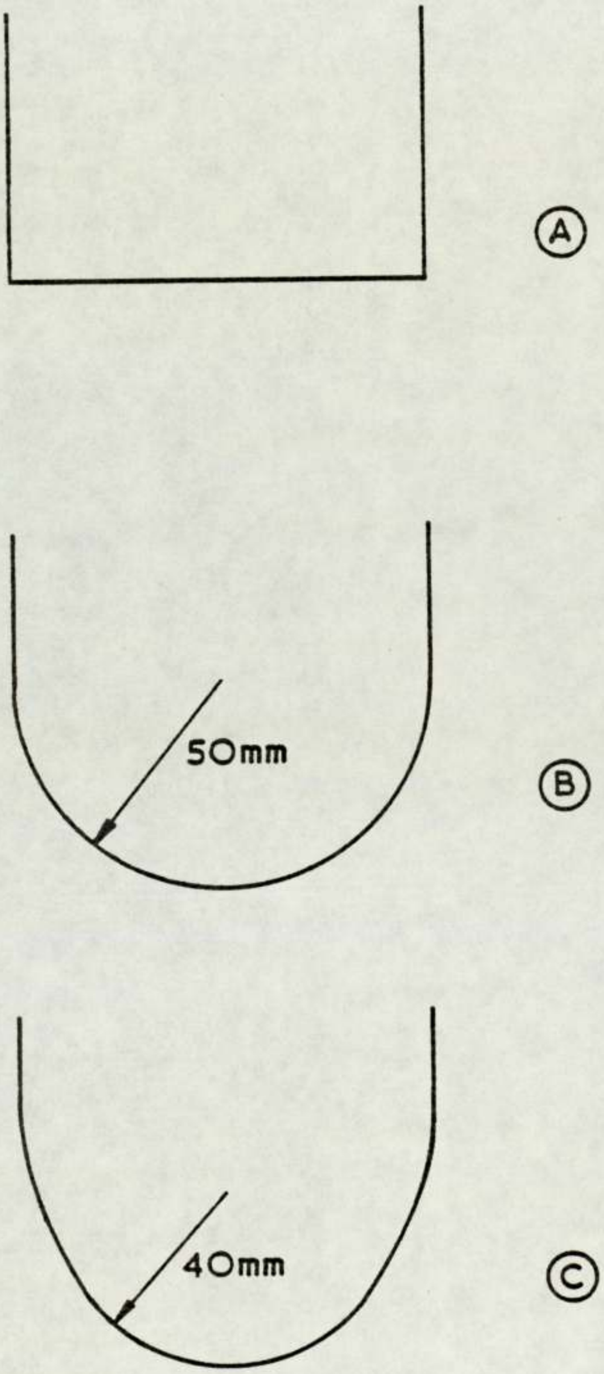


FIG 5

The slag cover was simulated by partially expanded polystyrene beads. A number of slag materials were tested, including vermiculite, but the beads gave the best representation of the granular yet sticky nature of the desulphurisation slag.

For each mouth shape the percentage slag removal for a given pouring time was determined.

TABLE 26

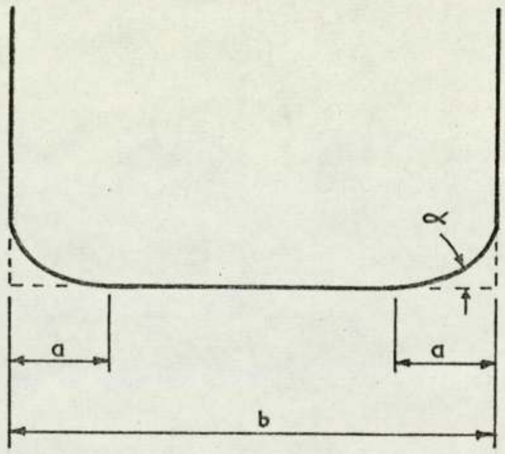
DEPENDENCE OF SLAG REMOVAL ON TORPEDO POURING TIME

Torpedo Mouth	Pouring Time (sec)	% Slag Removal
Rectangular	35 - 40	80
	65 - 70	48
50 mm. radius	35 - 40	80
	65 - 70	43
40 mm. radius	35 - 40	70
	65 - 70	33

There is a slight reduction in slag removal ability for the narrower torpedo mouths, but in terms of the plant problem this difference is not very significant.

The effect of pouring rate is very strong indeed. Halving the emptying time almost doubled the quantity of slag removed.

The ability to remove rafts of slag (simulated by broken pieces of expanded polystyrene sheet) was studied in the model. The pieces were placed in the torpedo with the granular slag cover. In the experiments all initial conditions were maintained constant and only the pouring rate was varied.



% Mouth width curved

$$= \frac{2a \times 100}{b}$$

Angle of Curvature = α

MODIFICATION TO TORPEDO MOUTH

FOR BETTER POURING CHARACTERISTICS

TABLE 27

EFFECT OF TORPEDO MOUTH SHAPE ON SLAG LUMP REMOVAL

Torpedo Mouth	Pouring Time (sec)	% Slag Lump Removal
Rectangular	35 - 40	33.3
	65 - 70	20.0
50 mm. radius	35 - 40	13.3
	65 - 70	6.7

Whilst it was recognised that simulations of this type are prone to error and could not be directly related to plant operation the difference between the two designs was sufficiently large to expect a real benefit to operations if the larger rectangular mouth was introduced.

A disadvantage noted for the rectangular mouth design was that it gave a very wide pouring stream with a tendency for splashing to occur from its edges. This lack of control would be a handicap to plant operation. The introduction of a slight curvature to the mouth produced a controlled stream without decreasing the slag removal efficiency. A number of stream measurements were taken from the model to illustrate this effect.

TABLE 28

EFFECT OF TORPEDO MOUTH CORNERS ON STREAM CONTROL

% Mouth Width Covered by Curved Edge (both sides)	Edge Angle to Horizontal (Degrees)	Stream Width (mm) Vertical Distance from Lip	
		40 mm.	70 mm.
8.8	26	40	20
8.0	30	50	30
6.8	35	65	40
6.3	51	70	45
5.5	55	75	50

These data are plotted in Fig. 59. It was evident that only a small modification to the mouth gave the desired stream conditions.

The results of this work were later confirmed by further model studies at the Steel Corporations Teesside Laboratories, (ref. 68).

As a result of the work reported a modified mouth design was introduced to the torpedoes. A change of this type required a major strengthening of the torpedo body and therefore took several years for a significant number to be altered. The on-plant assessment of the rectangular mouth is discussed below.

TORPEDO POURING STREAM CONTROL

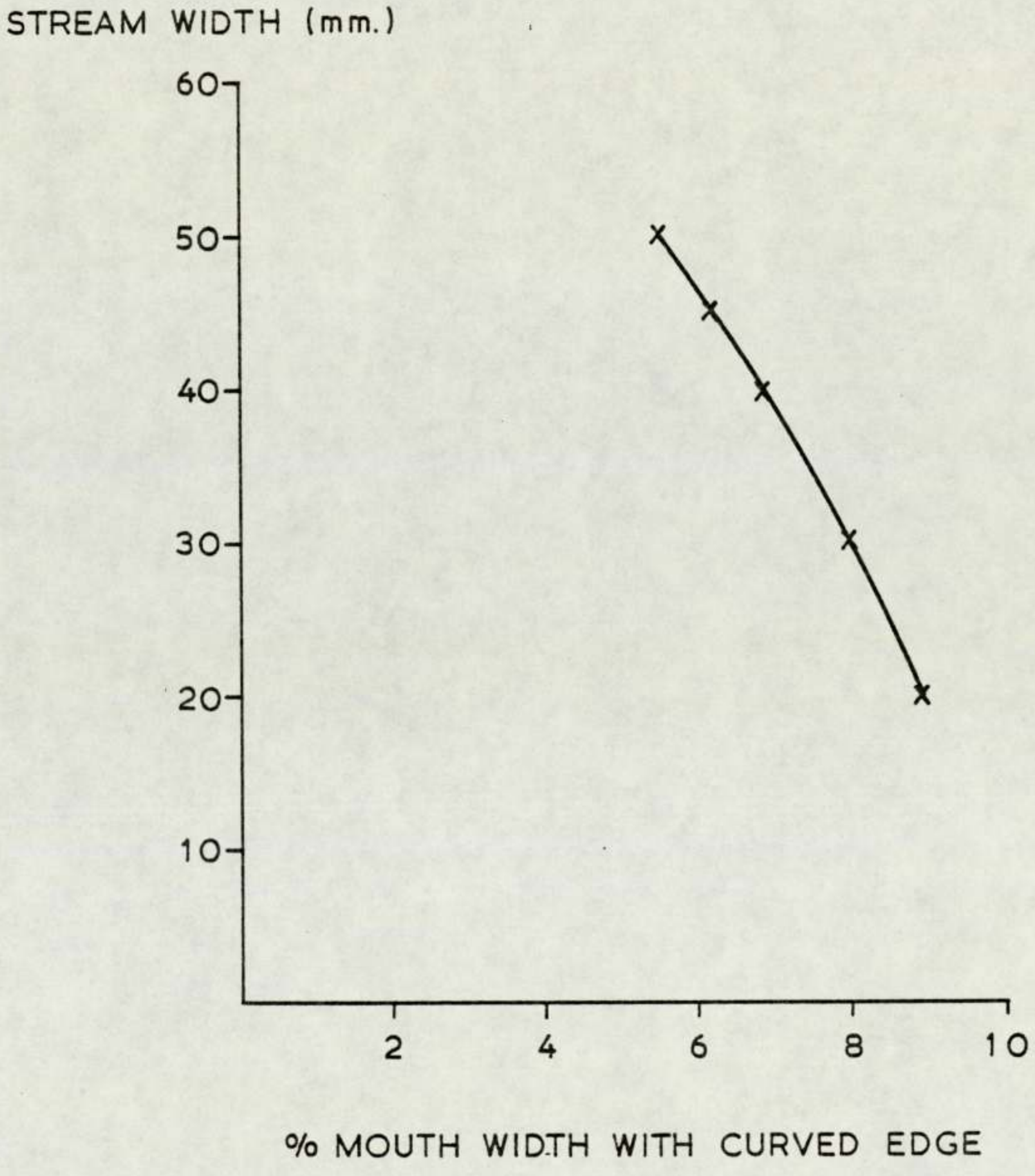


FIG. 59

7.3. Plant Data on Rectangular Mouth Operation

The effectiveness of the modified mouth in increasing the ease with which slag is removed is difficult to evaluate from plant data, since no direct measurements can be taken. However the aim of the work was to decrease the rate of slag build up in the torpedo so that better desulphurisation efficiencies could be obtained or a greater frequency of torpedo treatment be permitted. Many factors affect the desulphurisation efficiency other than torpedo condition, therefore an attempt was made to identify any changes in torpedo tare weight (i.e. build up) resulting from the use of the reactangular mouth torpedoes.

Earlier tests at the Scunthorpe Works had shown that a good relationship could be obtained between the frequency of desulphurisation and the tare weight of a torpedo. If the rectangular mouth was effective, this relationship should be invalid or decreased in value.

Data were recorded for a number of torpedoes with both round and rectangular mouths simultaneously over a six month operating period. Typical examples are given in Tables 29 and 30, for the round and square mouth designs. In the Tables, percentage desulphurisation refers to the number of times per day a torpedo was treated relative to its number of journeys between the ironworks and the steelplant. When examining data of this type simple graphs are often unsuitable as indicators of trends. For this reason the data has been plotted on a cumulative - sum basis; i.e. for each point the difference from a base value (normally the mean of the set) is calculated, consecutive points then take the value of that difference plus the sum of the preceding differences. The cu-sum graphs for the torpedoes are given as Fig. 60.

For the round mouth torpedo there is a close relationship between desulphurisation frequency and tare weight, thus confirming previous findings. However for the square mouth torpedo there is a significant delay (c. 16 days) between the increase in desulphurisation and the increase in tare. This indicates that the square mouth is helping to reduce slag build up, but that the effect is not being maintained for a long period.

Observations made at the steelplant hot metal pouring station gave an explanation of what was happening. The square mouth corner angles were added after the main body of the mouth had been built, and these corners were eroding after only a short service life. As a result, to obtain a good metal stream during pouring it was necessary to reduce the pour rate. It has been shown that this has a large effect on slag removal ability. This aspect of construction was discussed with plant management and steps are being taken to remedy the problem.

It should be noted that because of the large number of torpedoes involved and their long service life developments of this type take many months to evaluate and complete.

TABLE 29

DAILY TARE WEIGHT AND DESULPHURISATION DATA FOR SQUARE MOUTH TORPEDO (NO. 21)

Tare (t)	Cu-Sum Value	% Desulph.	Cu-Sum Value	Tare (t)	Cu-Sum Value	% Desulph.	Cu-Sum Value
211	15	33	17	221	80	-	-
216	25	-	-	223	83	-	-
230	21	25	42	220	89	25	- 93
216	31	-	-	222	93		
220	37	-	-	224	95		
221	42	33	59	237	84		
218	50	50	59	235	75		
219	57	-	-	236	65		
-	-	-	-	240	51		
220	63	-	-	242	35		
251	38	-	-	244	17		
227	37	33	76	250	-7		
219	44	66	50	251	-32		
219	51	33	67	249	-55		
223	54	100	17	249	-78		
225	55	25	42	242	-94		
224	57	-	-	240	-108		
224	59	-	-	234	-116		
222	63	-	-	232	-122		
236	53	100	-12				
229	50	66	-28				
222	54	100	-78				
234	46	-	-				
224	48	-	-				
222	52	75	-103				
218	60	-	-				
219	67	65	-118				
218	75	-	-				

Tare Weight: Cu-Sum Base = 226t.

% Desulph. Treatments: Cu-Sum Base = 50%

TABLE 30

DAILY TARE WEIGHT AND DESULPHURISATION DATA FOR ROUND MOUTH TORPEDO (NO. 11).

Tare (t)	Cu-Sum Value	% Desulph.	Cu-Sum Value	Tare (t)	Cu-Sum Value	% Desulph.	Cu-Sum Value
214	-2	25	25	220	194	75	150
212	-6	33	42	222	200	38	162
215	-7	40	52	212	196	66	146
214	-9	50	52	211	191	61	135
221	-4	83	30	209	184	56	129
222	+4	45	35	209	177	54	125
235	+23	45	40	208	169	61	114
228	36	-	-	210	163	66	98
232	52	-	-	211	158	56	92
224	60	35	55	212	154	54	88
228	72	33	72	209	147	66	72
219	75	-	-	219	150	60	62
224	83	48	52	213	147	57	55
223	90	37	65	213	144	60	45
239	113	33	82	207	135	60	35
226	123	33	99	209	127	66	19
221	128	-	-	206	117	57	12
235	147	37	112				
224	155	33	129				
240	179	-	-				
218	181	37	142				
221	186	33	159				
214	184	-	-				
212	180	-	-				
220	184	-	-				
219	187	-	-				
219	190	37	172				
217	191	45	177				

Tare Weight: Cu-Sum Base = 216t.

% Desulph. Treatments; Cu-Sum Base = 50%

DAILY TARE WEIGHT AND DESULPHURISATION DATA

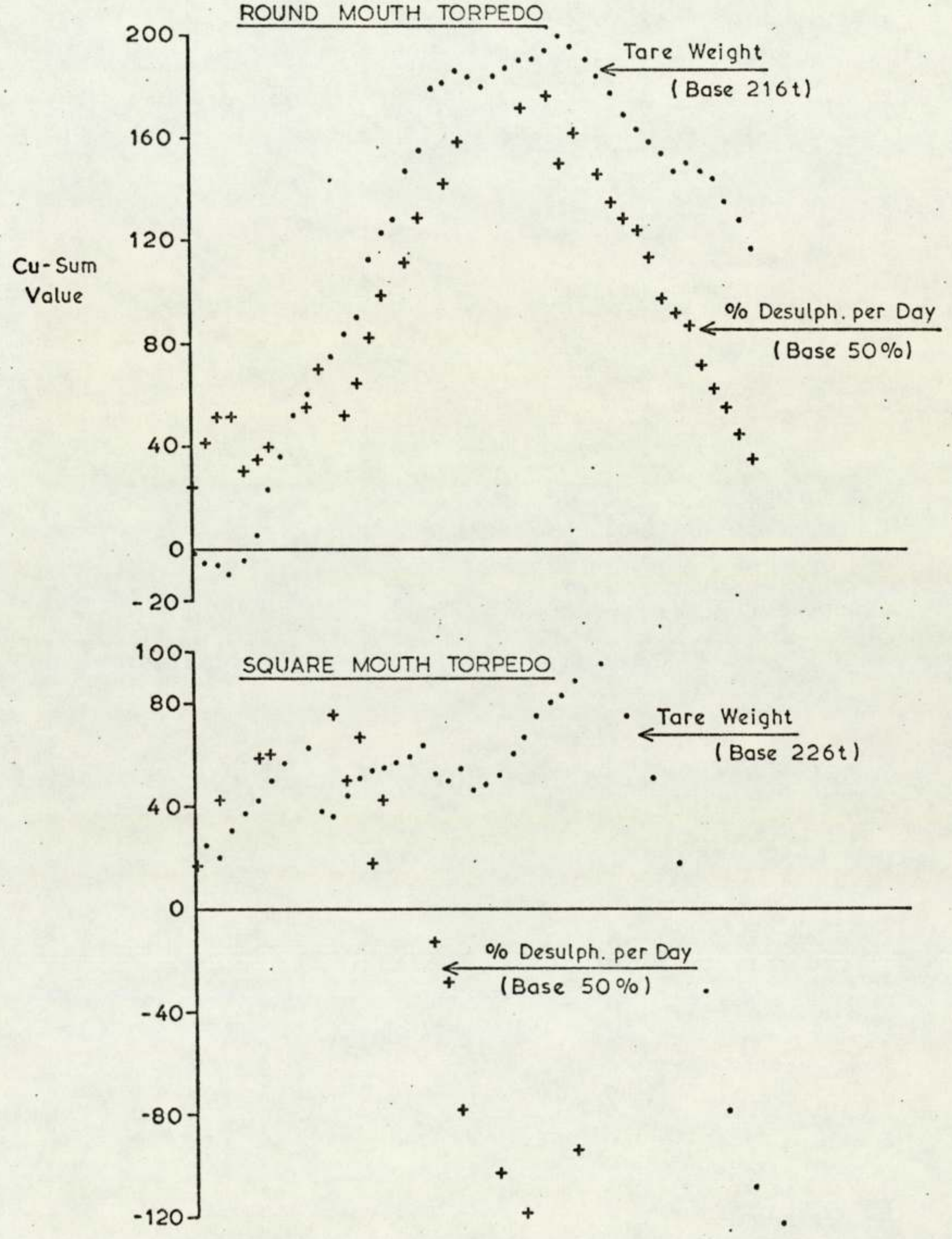


FIG. 60

8. THE USE OF SODA ASH AS A SLAG FLUX DURING TORPEDO DESULPHURISATION

8.1. Introduction

At the Appleby-Frodingham Works, in an effort to reduce the torpedo skull problem, many attempts have been made to produce a more fluid slag in the torpedoes both prior to and after the desulphurisation process. None of these have been successful. After studying the skull formation mechanism more closely, it was decided that the simultaneous addition of a flux with the desulphurising agent was the method most likely to give the required result. In terms of cost, availability and fluxing efficiency soda ash was selected as the fluxing agent.

8.2. Procedure

To carry out the trial a small pneumatic dispenser (capacity 1.5 m^3) was set up alongside the CaD injection equipment and its discharge time coupled with the CaD line just before the lance coupling point.

The basic procedure was to add 10% by weight of soda ash to the CaD mixture if the tare of the torpedo being treated was greater than 220t. This limit was set to reduce the danger of refractory attack by the soda ash which would undoubtedly occur in a clean torpedo. During the trial period this procedure was modified on some occasions to treat specific torpedoes on each Blast Furnace to Steelplant journey whether desulphurisation would normally be required or not.

8.3 Operating Problems

The soda ash dispenser was set up for operation with a 6 mm. orifice at its base to give the flow control required. After only two treatments this orifice blocked. The soda was found to contain lumps up to 10 mm. long. Refilling the dispenser with soda ash screened through a 1 mm sieve and increasing the orifice diameter to 8 mm. did not solve the problem, which was then thought to be due to the moisture content of the soda being used. However the use of soda specially delivered in polythene/polypropylene bags gave no improvement. Up to this time I.C.I 'Light Grade' soda had been used because its particle size was the most suitable for the dispensing operation and its flow characteristics were compatible with CaD. It was then realised that 'Light' soda has needle shaped particles which would be very prone to compacting, especially in the dispenser region between the fluidising cone and the orifice. To test this theory Granulated soda ash was used. It flowed freely from the dispenser and no further flow problems were encountered.

When soda ash is injected into iron a considerable amount of fume is generated. When the 'Light' soda was used this fume was not excessive, unfortunately the different characteristics of the Granulated material increased the fume evolved, and this brought the trial to a premature end.

NONE WENT IN

WHY

8.4. Trial Results

During the trial period fluxing was attempted on 116 torpedoes. Of these 66.4% were successfully treated and 6.9% partially treated; the majority of the failures were in the early stages of the trial. The average flux ratio was 9.8% soda ash to 90.2% CaD. In total 20.28t. of soda ash were dispensed. Of the torpedoes passing through the desulphurisation unit 32% were treated with soda ash.

8.4.1. Hot Metal Pouring

Observations were made of the pouring characteristics of the three types of slag occurring in the torpedoes over the trial, i.e. Blast Furnace, Desulphurisation, and Desulphurisation plus soda ash slags. The soda ash treated slag gave a bright soda flame during pouring, which at times obscured the view of the torpedo pour operator.

The soda did not change the form of the desulphurisation slag, but was observed to have fluxed its associated Blast Furnace slag. A difference in pouring characteristics could not be seen because of the strong influences of the other factors involved (Sect. 7).

8.4.2. Torpedo Tare Weights

The effect of the soda treatment on tare weight was assessed by analysis of both the weekly average data and examination of individual torpedo records.

Over the trial period the weekly percentage of total torpedoes desulphurised using carbide varied from 31 to 44%, Fig. 61, averaging 35.8%, which is close to the normal level. The torpedo tare weights over this time were consistently low, Fig. 62. A record of the tares for two torpedoes is given in Figs. 63 and 64. In the first the tare weight increases with normal desulphurisation treatments until when soda ash was used the tare stabilises, although at a high level. In the second during continued treatment with soda ash the tare remains virtually constant.

AGAINST THESSIEN REMARKS ??

The soda ash added with the CaD was not sufficient to modify the form of the slag and therefore its pouring characteristics. Theoretically some change should have occurred. It was evident from the pouring observations that even under the turbulent conditions of injection the reacted soda ash was mixed with the much larger, relatively solid, bulk of the carbide slag.

– HOW MUCH NEEDED

WHAT THEORY

No in BF slag you said earlier (overlap)

The treatment did appear to have some effect on internal skull formation. Unfortunately, because of the fume problem, the trial period was not long enough for the total effects to be established.

WHY NOT
ONE TORPEDO
ALL TIME

It was therefore recommended that the trial should be repeated on a plant which had a fume extraction and cleaning system.

WEEKLY PERCENT TORPEDO DESULPHURISATION

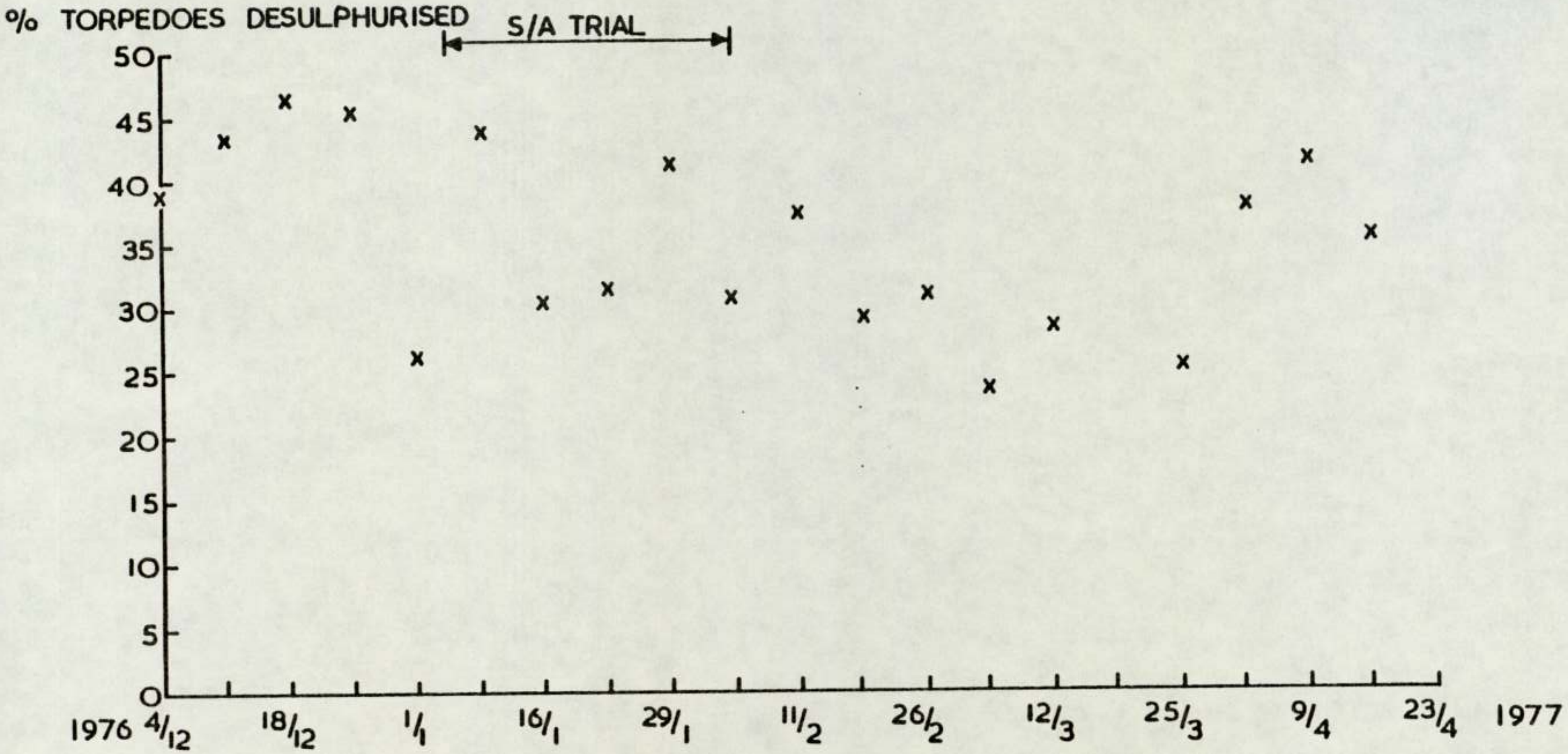


FIG 61

WEEKLY AVERAGE TARES

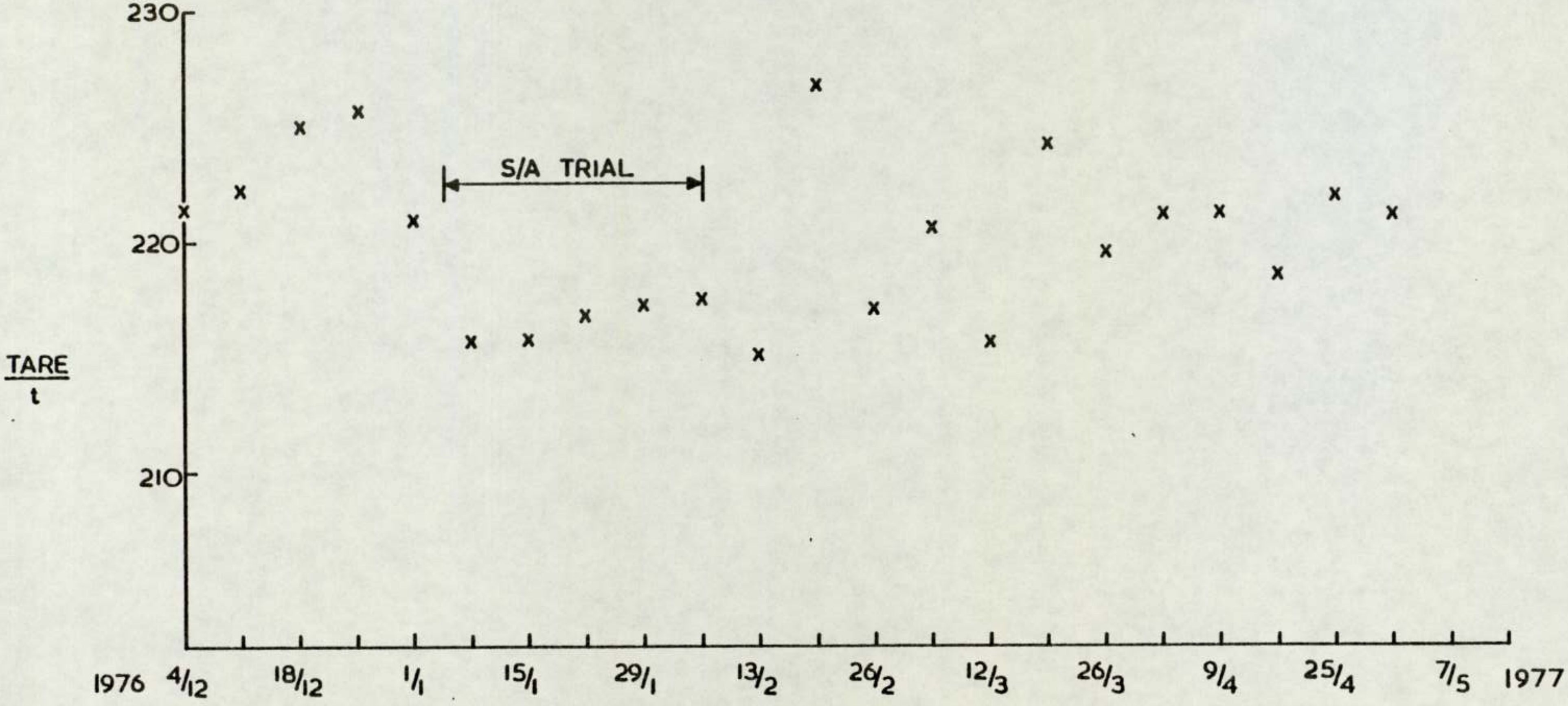


FIG 62

VARIATION IN TORPEDO TARE WT.

TORPEDO Nº2 FROM 21·1·77 TO 4·2·77

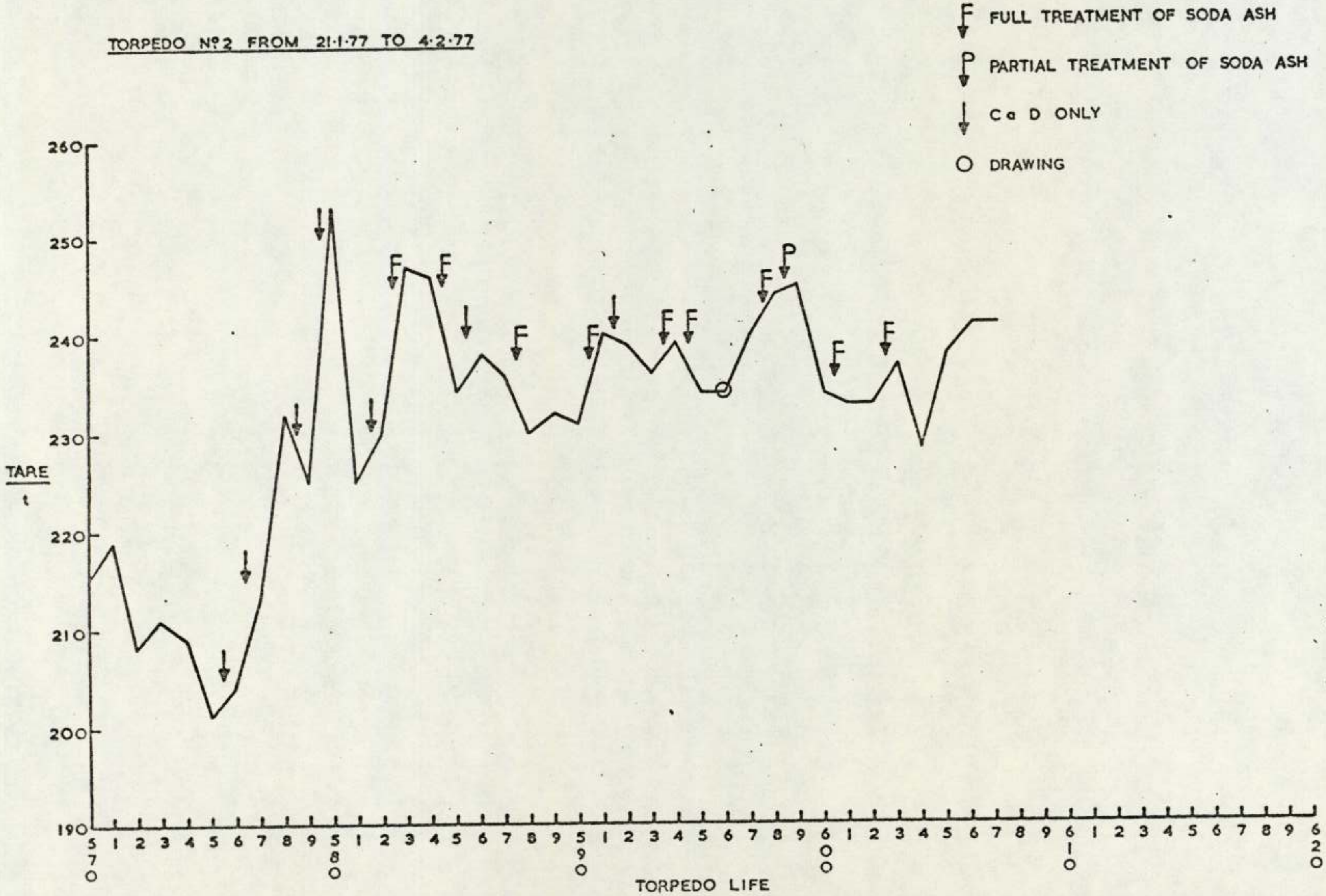


FIG 63

VARIATION IN TORPEDO TARE WT.

TORPEDO No 8 FROM 18·1·77 TO 4·2·77

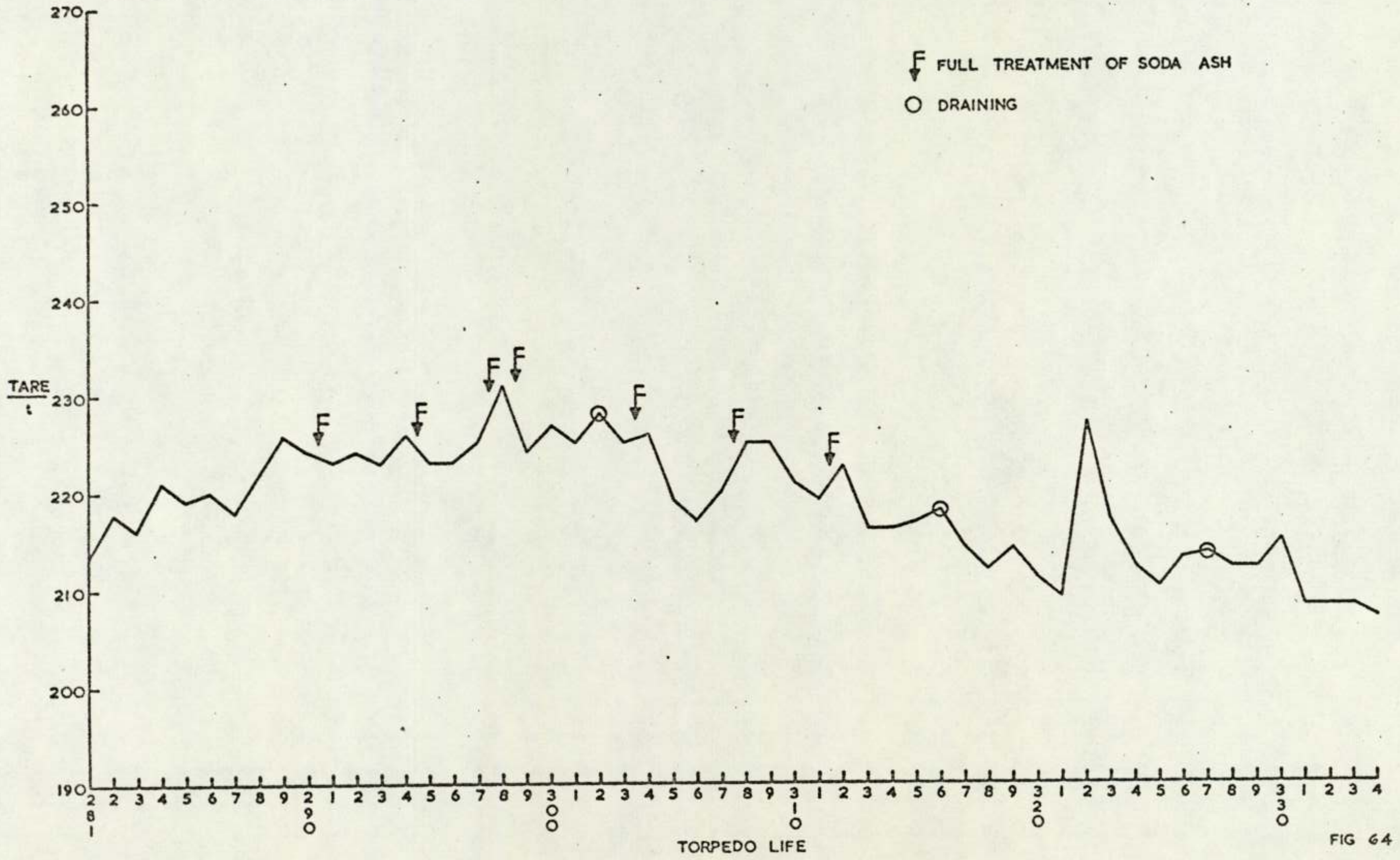


FIG 64

9. TRANSFER LADLE SLAG SKIMMING USING GAS BUBBLING

9.1. Introduction

Iron desulphurisation processes usually transfer sulphur from the iron into a slag which floats on the metal surface. At the Appleby-Frodingham Works for example, this slag may contain in excess of 3%S. If this slag is charged to the steelmaking vessel it becomes part of the overall steelmaking slag reaction and the effort and expense of desulphurisation has been wasted. When torpedo desulphurisation is used there are two methods available to prevent slag carryover into the vessel: 1) retain it in the torpedo or 2) remove from the transfer ladle before the metal is charged into the convertor.

The practice of slag retention in torpedoes using tapholes has been widely publicised by Dofasco. On the basis of their success a taphole configuration for the Appleby torpedoes was designed in the laboratory using water models. However when put into operation it soon became apparent that the system was not practicable under Appleby-Frodingham Works conditions. The taphole itself could not be kept open during the desulphurisation process and the retained slag could not be drained out. The success of Dofasco is due to their torpedo shape. These have a small length to diameter ratio and a sharp angle between the mouth and torpedo ends. This design gives a large freeboard during injection and facilitates slag draining.

1kMP

The normal practice at Appleby-Frodingham and at most of the world's steelplants is to use a mechanical rake to pull the slag from the transfer/charging ladle before charging the vessel. The efficiency of this process is dependent upon the type of slag, i.e. its fluidity, and the power and manoeuvrability of the skimming machine (slag rake), and the skill of the operator.

To improve the efficiency of the skimming operation the Hoesch steelplant introduced and developed a process whereby gas is bubbled through porous plugs set at the back of the ladle (ref. 43). When the gas bubbles break at the surface the slag is driven across the metal surface toward the skimmer blade. A secondary part of this development is to feed a 'coagulant' on to the clear metal surface behind the slag. This material, normally pearlite (a naturally occurring mineral) based, acts like a 'dish cloth' and sweeps a batch of slag, larger than the skimmer could normally remove, from the metal surface. During a visit to Hoesch this procedure was seen to be very successful on the ladle slags which they produce. The ladles appear to carry only a small volume of blast furnace slag and then the Galag (magnesium impregnated coke) process is used for desulphurisation. Galag produces a very small slag quantity compared with the calcium based processes, and it is normally of a hard, crusty nature, i.e. it lends itself to being moved easily across the metal surface.

Very high S slag

To determine the effectiveness of the bubbling process on other slag types, in particular those which occur at Appleby-Frodingham a series of model experiments were carried out. The results with respect to slag removal were used to estimate the possible effects on skimming time and steel sulphur levels.

9.2. The Model

The model was constructed to 1/20th scale from perspex sheet. Although porous plugs are normally used for the process, their safety aspects give some cause for concern, especially at Appleby-Frodingham where the hot metal passes directly over the main control area. For this reason the model work was done using a lance, Fig. 65.

criteria
m. Sl

Two types of slag were simulated: blast furnace slag, by using a heavy oil; and desulphurisation slag by using wet polystyrene beads. The latter is granular yet highly cohesive and as such was judged to be the most suitable material.

The process is based on the forces produced by the bubbles as they rise and break at the surface. For a water model this is difficult to simulate with any degree of accuracy in terms of definite modelling criteria. The range of gas rates used was selected on the basis of a visual estimation of surface area of metal exposed, (as seen at Hoesch) and to give a good range in terms of the model's ability to accept gas without excessive splashing.

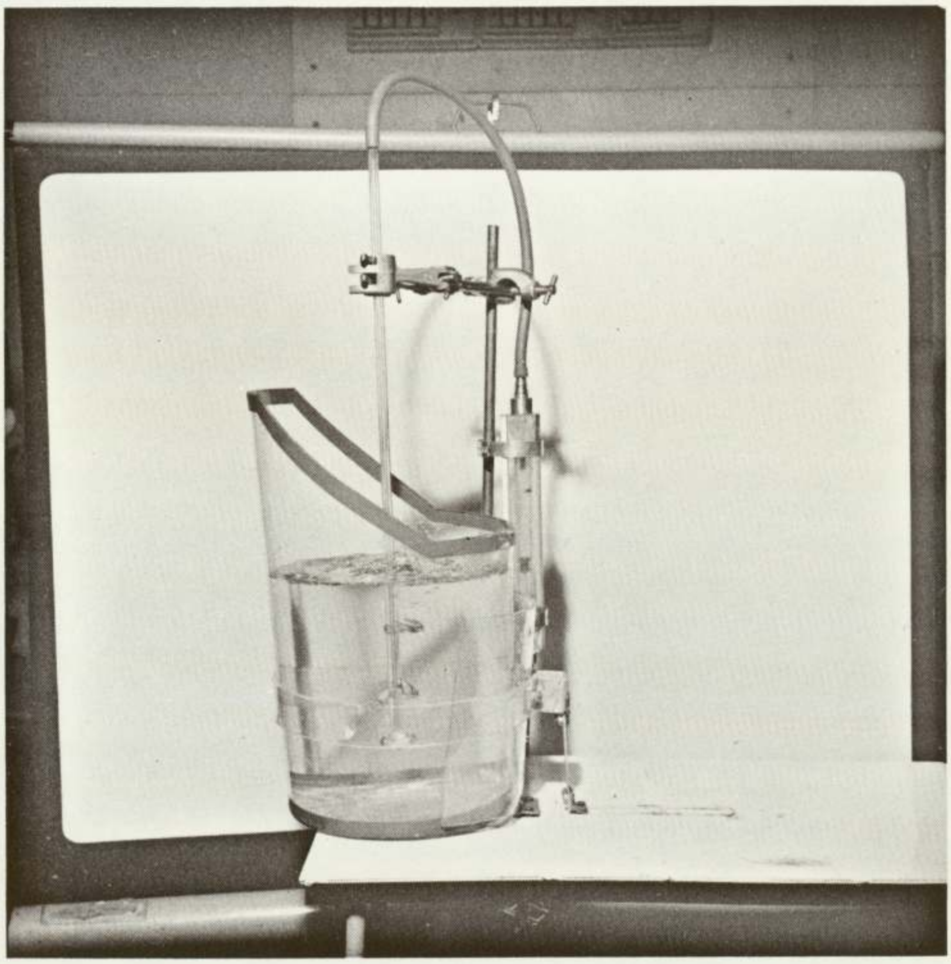


FIG. 65 - GENERAL VIEW OF TRANSFER LADLE MODEL

The skimming blade was formed from aluminium strip. It was hand operated in order to give the necessary control over its movement in all directions without recourse to complex equipment. Particular attention was paid to the withdrawal speed, and hence the wash characteristics, of the blade.

9.3. Procedure

For each experiment the ladle was filled with water equivalent to 260t. of metal. The model was then tilted to an angle of 15° to the vertical (the normal skimming position on plant for this weight of metal). The slag was then distributed evenly on the metal surface. For simulation of blast furnace slag 0.35 l. of oil was used, for desulphurisation slag 0.54 l. of the wet expanded beads was applied.

Wt of
Slag in
0.35 L oil
Related to
Plant ??

The parameters varied in the experiments were:

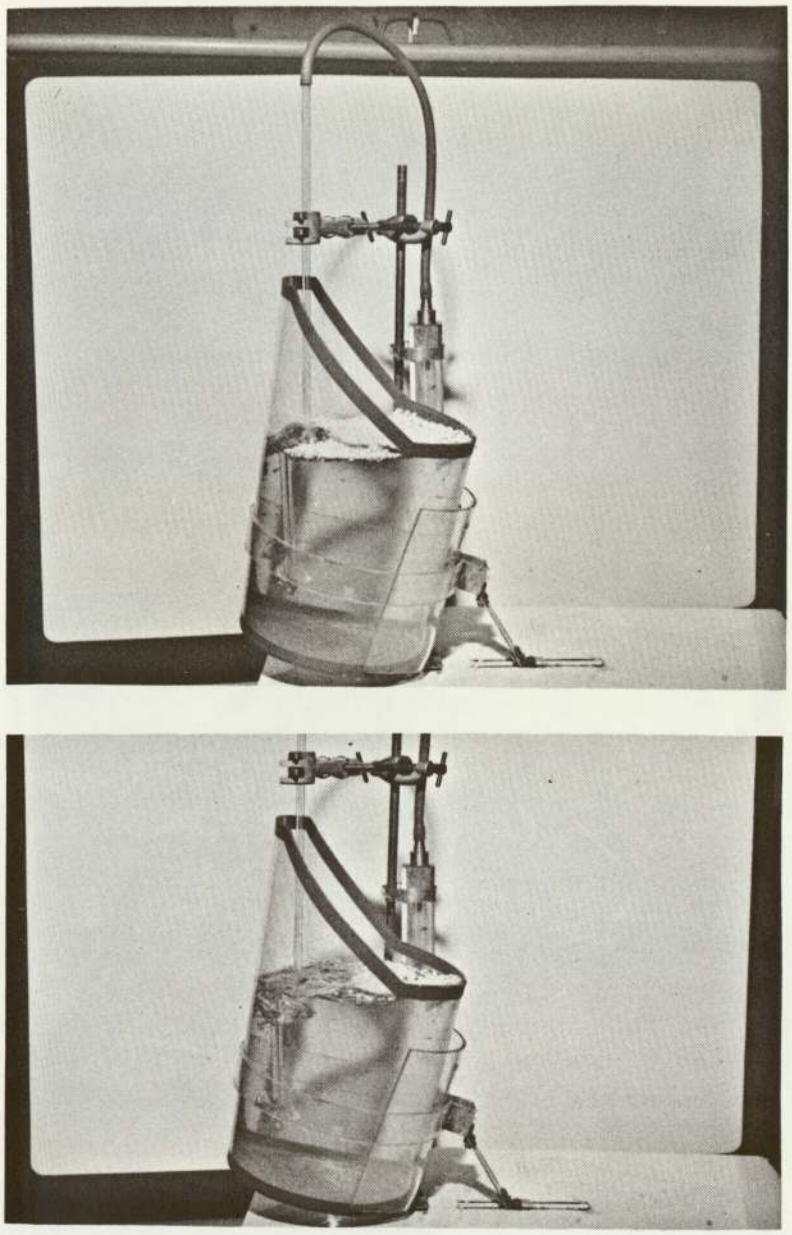
a) Lance immersion depth
b) Gas flow rate
c) Number of skimming strokes

The latter was repeated with and without gas for each slag type.

9.4. Results from the Model

9.4.1. Desulphurisation Slag Removal

The effect of gas bubbling on a desulphurisation type slag is shown in Fig. 66.



"Position of slag on surface as skimming operation progresses."

(a)

(b)

(c)

FIG. 66

As the slag is removed by skimming that remaining is forced toward the ladle lip by the gas.

The amount of slag removed for skimming

a) without gas

b) with varying gas rates at 25% lance immersion
50% lance immersion
75% lance immersion

is given in Table 31, and in Figs. 67, 68, 69. When the gas was used the percentage slag which could be removed increased from 85.2 to 99.1% in the best case. Alternatively the maximum slag removal which could be obtained without the aid of gas was achieved approximately 3 to 4 minutes quicker.

9.4.1.1. Lance Immersion Depth

Immersion depths of 25% and 50% produced no significant difference in the amount of slag removed. The deeper immersion of 75% allowed the higher levels of removal ($>$ 90%) to be achieved more quickly however this difference disappeared as the very small slag volumes were approached.

9.4.1.2. Gas Flow Rate

As was expected increased gas flow rate increased the slag removal for a given number of skimming strokes. The greater the surface turbulence at the back of the ladle the greater was the tendency for slag to be driven into still areas from where it could easily be removed.

TABLE 31

MODEL RESULTS FOR DESULPHURISATION SLAG REMOVAL

(a) No Gas Bubbling

No. of Skimming Strokes	% Slag Removal
15	64.8
25	76.9
40	85.2

(b) 25% Lance Immersion

Gas flow (l/min)	Skimming strokes	% Slag Removal
1	15	75.9
1	25	87.0
1	40	95.4
2.5	15	74.2
2.5	25	85.2
2.5	40	96.3
5	15	74.2
5	25	90.7
5	40	98.0

(c) 50% Lance Immersion

Gas flow (l/min)	Skimming strokes	% Slag Removal
1	15	74.2
1	25	85.2
1	40	94.2
2.5	15	75.8
2.5	25	85.2
2.5	40	96.3
5	15	74.2
5	25	85.2
5	40	98.0

TABLE 31 (Cont'd.)

MODEL RESULTS FOR DESULPHURISATION SLAG REMOVAL (CONT'D)

(d) 75% Lance Immersion

Gas flow (l/min)	Skimming strokes	% Slag Removal
1	15	74.2
1	25	88.9
1	40	94.8
2.5	15	74.2
2.5	25	90.7
2.5	40	98.0
5	15	77.8
5	25	90.7
5	40	99.1

% SLAG REMOVAL vs No. OF RABBLE STROKES

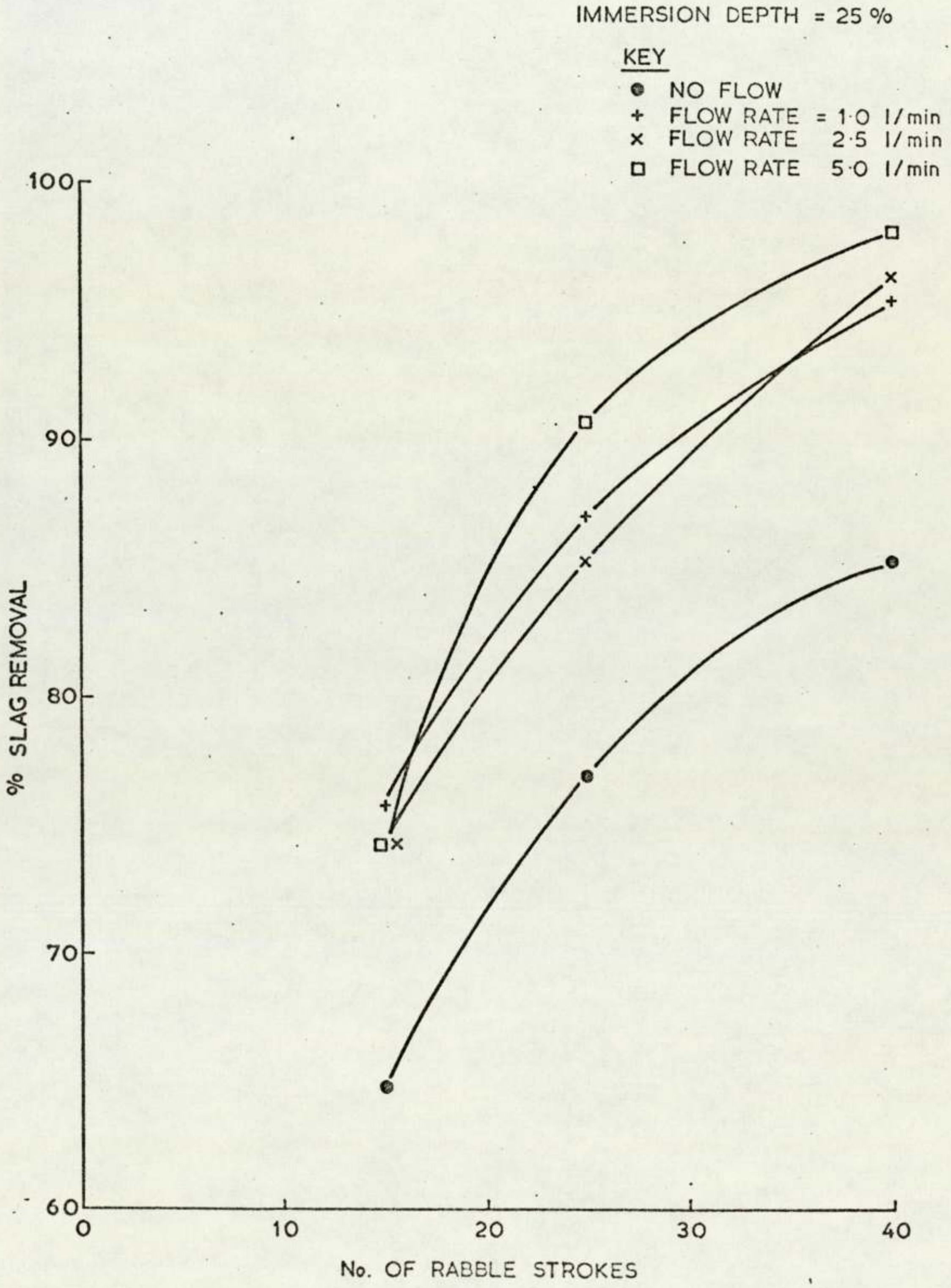


FIG.67

% SLAG REMOVAL / No. OF RABBLE STROKES

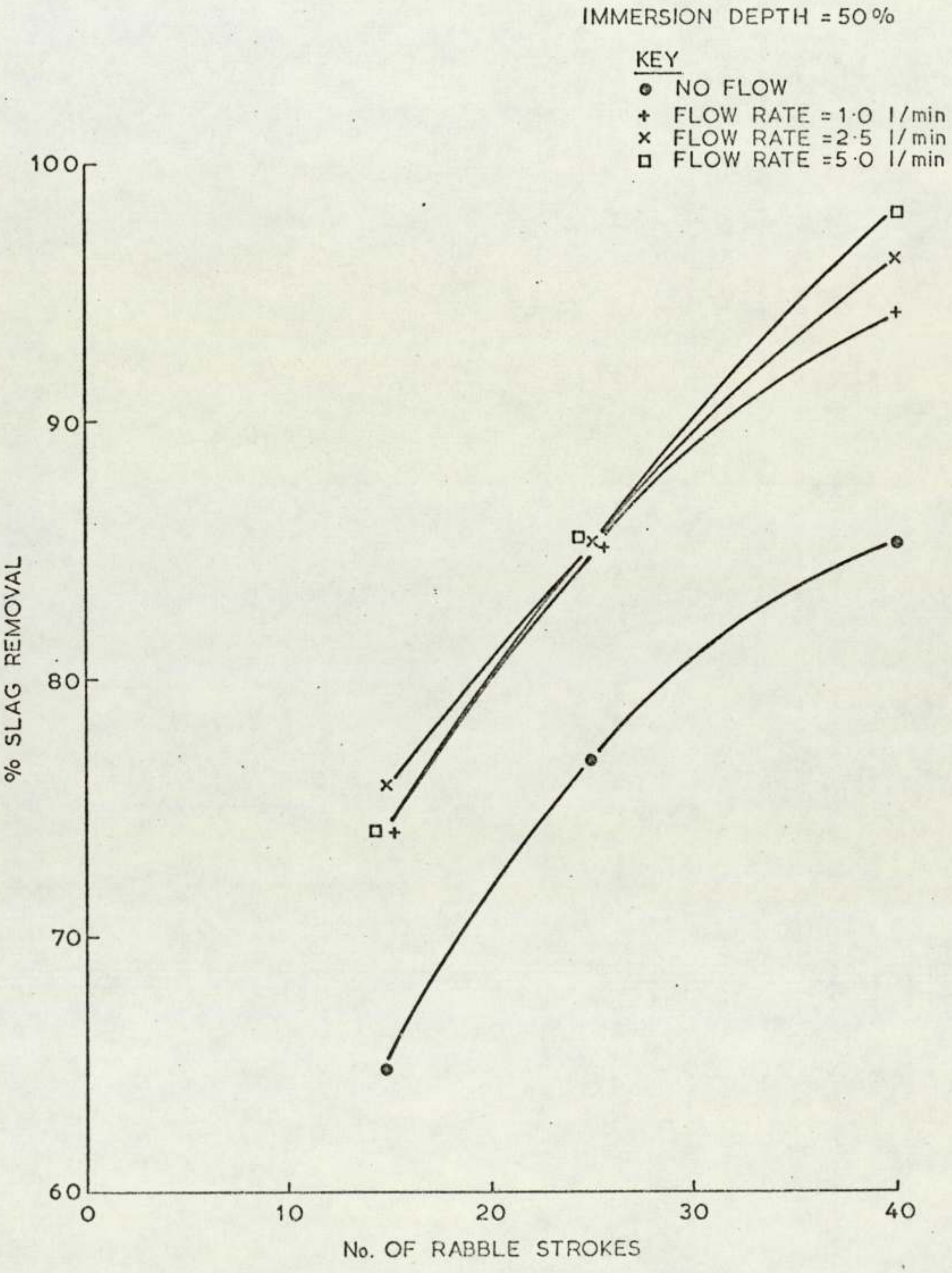


FIG. 68

% SLAG REMOVAL / No. OF RABBLE STROKES

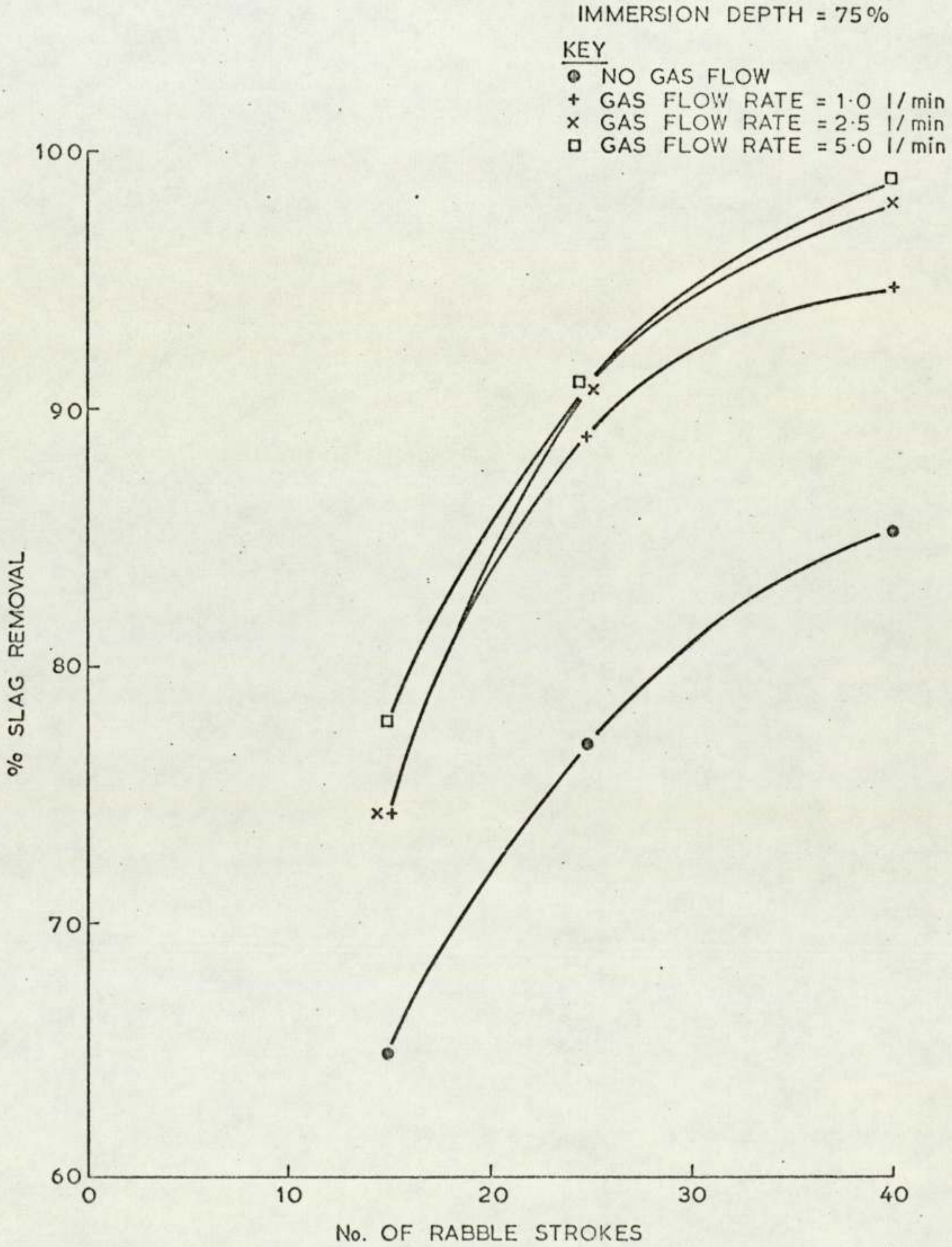


FIG. 69

9.4.1.3. Number of Skimming Strokes

required ??

The most significant feature of these results was that the degree of slag removal obtained using gas bubbling could not be achieved, certainly within any reasonable time, by merely increasing the number of skimming strokes.

what level needed

9.4.2. Blast Furnace Slag Removal

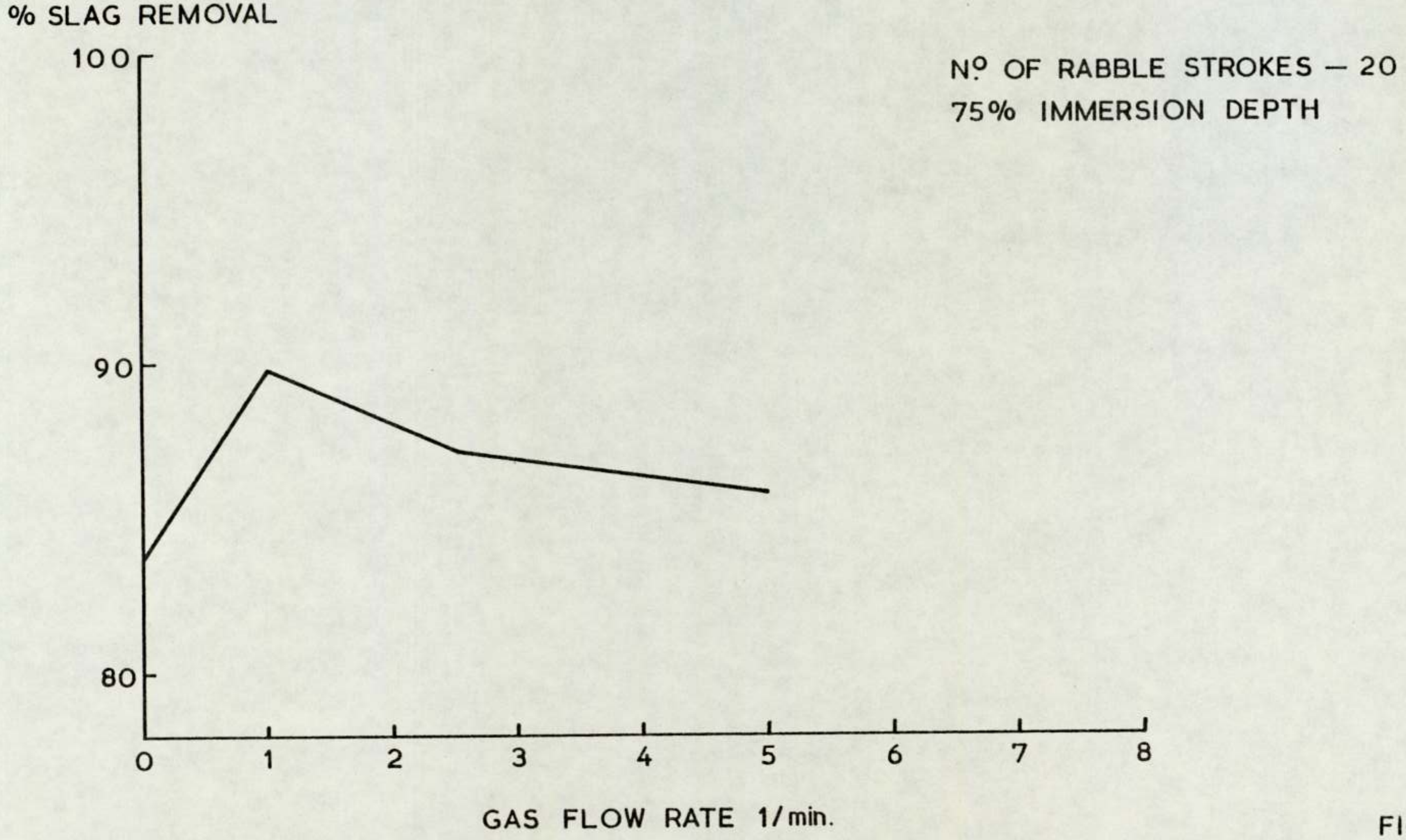
The slag removal obtained for the blast furnace slag simulation is given in Table 32, and Fig. 70. The primary purpose of the work was to examine desulphurisation slag, so the comparative data for blast furnace slag was limited to the case of 75% lance immersion.

Although oil has been used for slag/metal flow situations for this model work it was not sufficiently viscous and problems with splashing and emulsification were encountered which are known not to occur during plant operation.

Without the use of gas 83.6% slag removal was possible at 20 skimming strokes. Increasing the skimming time produced only a small benefit which could not be realised in practice.

Same as [illegible] DeS with gas.

The lowest gas rate enabled the slag removal to be increased to 89.8%. Higher gas rates produced emulsification and splashing which affected the results.



% SLAG REMOVAL VS GAS FLOW RATE

(BLAST FURNACE SLAG)

FIG. 70

9.5. Discussion of Model Results

The model clearly showed that for the most important case of desulphurisation slag removal, gas bubbling has the effect of driving the slag across the metal surface. For blast furnace slag the effect was not as well defined but practical experience of the problem plus the observations made of the model indicates that a significant benefit could be obtained given reasonable control of the gas rate used.

why

An important feature of the process should be that its greater efficiency should reduce the loss of iron during the skimming process. Under normal (non gas-aided) conditions a reduction of slag carryover to 0.5% of the metal weight may incur a yield loss of 0.5% of the metal, or greater.

9.6. Translation of Desulphurisation Slag Removal Results To Plant Operation

To illustrate the effects of slag carryover to the vessel and the real benefits to be obtained by an improvement in the skimming operation, the results for desulphurisation slag removal were input to a mathematical model (written by the author) for the prediction of steel sulphur levels.

The data were applied to a standard vessel charge, Table 33. The slag carryover to the vessel was taken from Table 31, as the mean of the values obtained at each gas flow rate at an immersion depth of 75%, Table 34.

Plant observations were carried out to relate skimming time to the number of strokes used, and this superimposed on the model results, Fig. 71. The effect of gas bubbling on steel sulphur level is shown in Fig. 72. It can be seen that the time saved by gas bubbling increases with increasing slag removal. At 25 skimming strokes for example the slag carryover is reduced from 1.33% to 0.57%, which reduces the steel sulphur level from 0.0375% to 0.0240%. To achieve this without gas would take an extra 8 minutes of skimming time. SO WHAT?

Although these results can only be approximate to the real situation because of the general basis of the model experiments, they do clearly demonstrate the scale of the benefit which may be obtained.

A typical sulphur balance for the B.O.S. process was shown in Fig.12. The case for good slag removal is further illustrated by the comparison of this input with that for a typical low sulphur charge,

i.e. hot metal at 0.005%S
scrap selected at 0.020%S
carryover slag 2.5 t. at 2.5%S

This is shown in Fig. 73.

before skimming

% SLAG CARRY OVER TO VESSEL vs No. OF RABBLE STROKES/PLANT RABBLING TIME

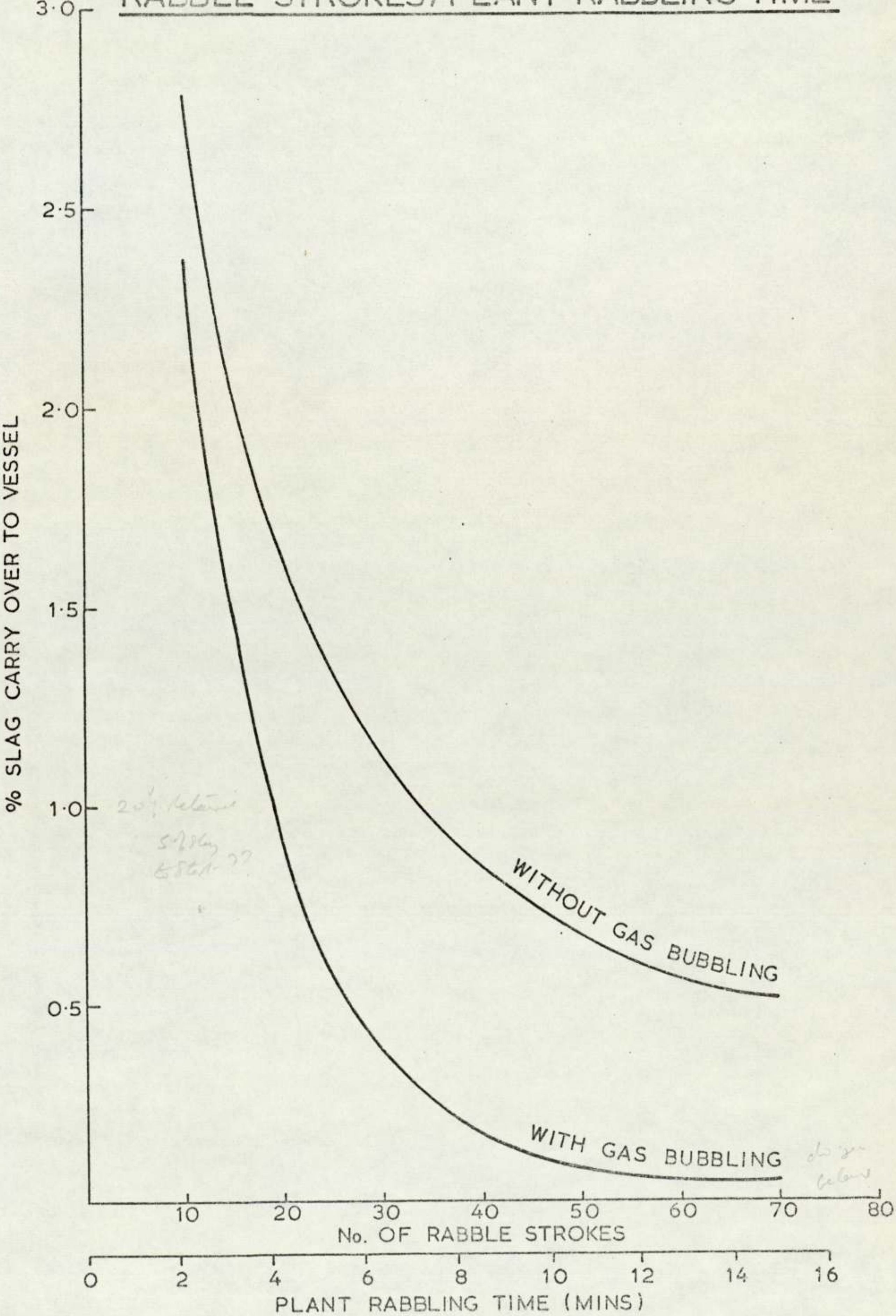


FIG. 71

% BATH SULPHUR vs No. OF RABBLE STROKES/PLANT RABBLING TIME

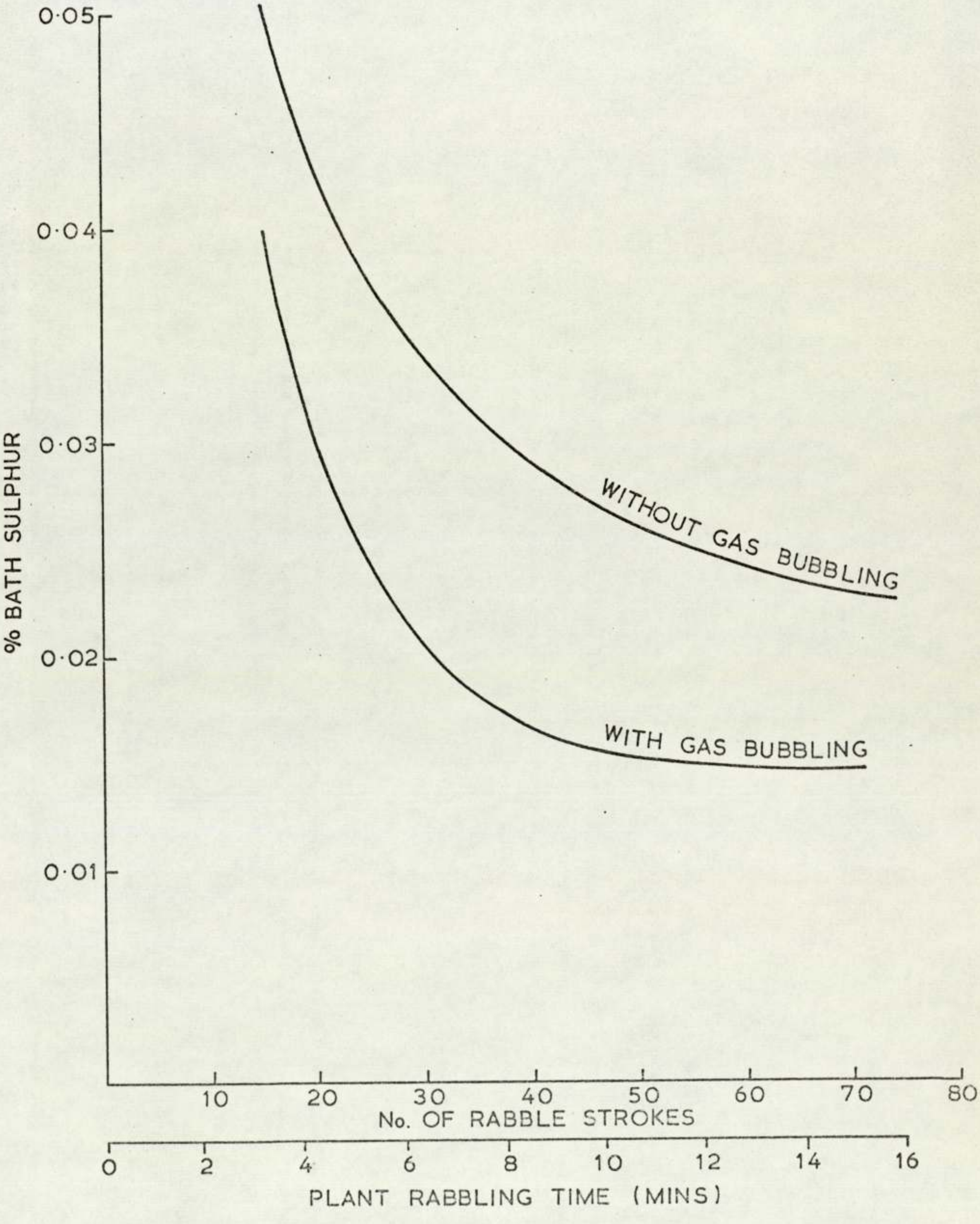


FIG. 72

COMPARISON OF B.O.S. CHARGE SULPHUR LOADS

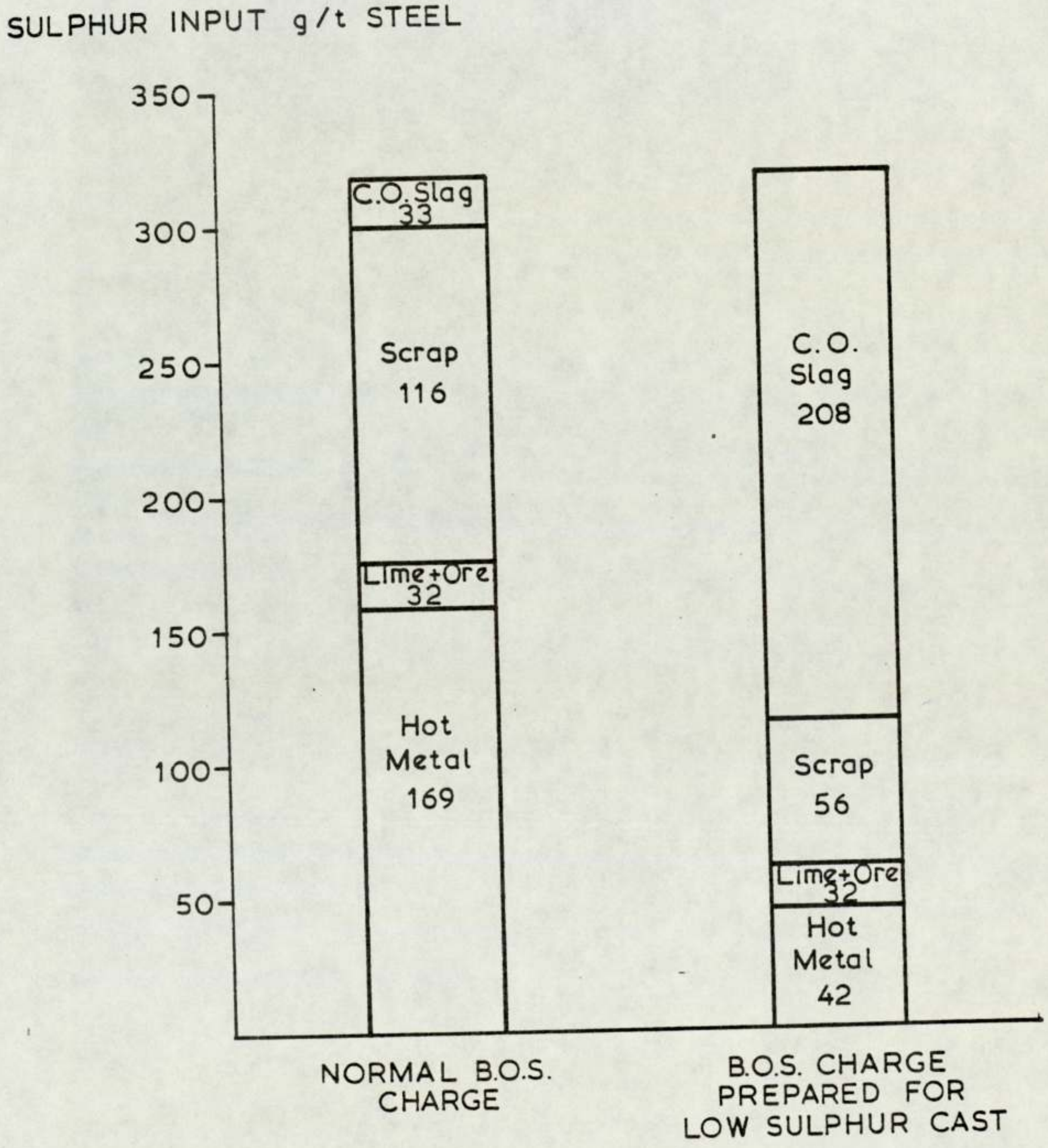


FIG. 73

TABLE 32

MODEL RESULTS FOR BLAST FURNACE SLAG REMOVAL

No. of Skimming strokes = 20

Gas flow rate (l/min)	% Slag Removal
0	83.6
1	89.8
2.5	87.1
5	85.8

TABLE 34

INTERPRETATION OF MODEL RESULTS

(a) % Slag Carryover

[illegible] = 2.5%?

No. of Skimming strokes	% Slag Carry Over	
	Without Bubbling	With Bubbling
15	2.0	1.4
20	1.6	0.9
25	1.3	0.6
30	1.1	0.4
35	1.0	0.2
40	0.9	0.2

(b) % Bath Sulphur

No. of Skimming strokes	% Bath Sulphur	
	Without Bubbling	With Bubbling
15	0.050	0.039
20	0.043	0.030
25	0.038	0.024
30	0.034	0.020
35	0.031	0.018
40	0.029	0.017

TABLE 33.

STANDARD B.O.S. VESSEL DATA USED FOR STEEL SULPHUR PREDICTION

Hot Metal	249 t.
Scrap	76.5 t.
Ore	5.8 t.
Steel	300 t.
Lime	23.4 t.
Vessel Sulphur Partition $\frac{(\underline{S})}{[S]}$	6.3
Blast Furnace Iron %S	0.058
Transfer Ladle %S	0.010
Scrap %S	0.045
Blast Furnace Slag %S	1.8
% Slag Carryover from Blast Furnace to Ladle	1.5

10. DISCUSSION - TORPEDO DESULPHURISATION

Repeat -

The Appleby-Frodingham torpedo desulphurisation plant injected calcium carbide and diamide lime (precipitated calcium carbonate) mixed in the ratio 70:30. The plant came on stream shortly after start-up of the main Anchor B.O.S. development. After a short operating period it became apparent that plant trials were needed to optimise performance. An integral part of these trials was accurate knowledge of the pre-treatment sulphur level.

At the time of the trials, standard practice was to take three iron samples from the blast furnace runner during the filling of each torpedo. The average analysis of these was then used as the starting point for desulphurisation. The iron in each torpedo could be from successive casts of a single furnace or from two furnaces. It was thought that this topping up operation added to the variation of iron analysis during casting could lead to stratification in the torpedo. A pre-treatment sample at the desulphurisation plant, taken from the top layer of metal, would therefore be unrepresentative. A sample unit was developed which could take samples simultaneously at different depths in the torpedo, and trials were carried out to clarify this situation. The results gave no evidence of stratification. Supportive laboratory model work confirmed this view as long as the iron casting rate was reasonably high and large changes in analysis did not occur when the torpedo was almost full.

It was noted that no significant metal analysis change took place between the blast furnace and the desulphurisation plant. It was concluded that for performance tests on desulphurisation the best estimate of metal analysis could be obtained from multiple samples taken at the blast furnace runner coincident with equal weights of metal cast. In practice this was not possible and the future trials were based on a single sample taken before treatment at the desulphurisation plant. This procedure then became standard plant practice.

Considerable experience was obtained in the practical operation of the plant as erected, but very little background information was available on the factors affecting plant performance. Primarily these are lance angle, desulphurant delivery rate, lance immersion depth and torpedo skulls, and are not readily amenable to examination under plant conditions. WHY The effect of each of these factors on performance is due to its influence on the degree of mixing of the iron during treatment. A perspex/water model was therefore built on which mixing efficiency could be measured. A study of the normal modelling parameters such as Reynold's No. resulted in a model size which could not be accommodated within the laboratory. In addition previous work at British Steel's Corporate Laboratories had illustrated the successful application of a modelling parameter based purely on relative rates of energy transfer. This technique was adapted for this work. The gas delivered through the model lance was equivalent to that used for material transport plus that from material decomposition in the iron.

The model gas rate calculated, based on the design capacity of the torpedo, could not be used because of excessive splashing. This paralleled the plant situation where very full torpedoes are part emptied before desulphurisation can begin, or in less extreme cases the material delivery rate is reduced and/or the lance is raised slightly. These aspects were to be examined individually so for the initial experiments the lance depth was maintained constant at the design level and the maximum possible gas rate was used. This gas rate was then adopted as the plant standard in the further work.

Metal flow patterns under different injection conditions were examined using partially expanded polystyrene beads. These gave a clear picture of what was happening inside the torpedo, especially with regard to the effects of a simple torpedo skull. Attempts to quantify the observations using a dye addition to estimate mixing time were only partially successful. The major problem being the inaccuracy involved in judging the time for even colouration of the water after the dye was added. Better results were obtained using a pH meter probe inserted at several points along the torpedo length and adding acid or alkali as the tracer.

The plant currently operates at a reagent rate of 60 to 80 kg/min. The results show that there is little benefit to be obtained by increasing this, in fact slightly lower levels could be tolerated as long as the time taken to make the addition did not become excessive. As the rate is reduced below 50 kg/min. the mixing efficiency is rapidly reduced.

Why will [illegible] mixture

The work clearly shows the importance of lance immersion depth on mixing efficiency. For sufficient energy to be imparted to the metal to produce mixing of iron in the torpedo end sections and homogeneity of analysis over the whole torpedo length the lance must always be immersed to the maximum depth possible. On the plant, the lance is driven to a fixed position above the ladle base. Therefore, lance immersion is synonymous with metal level in the ladle. A study of plant results showed that maintaining a high filling level would result in considerable financial savings with respect to carbide consumption.

The metal flow pattern and the rate of mixing obtained are symmetrical about the lance exit. The optimum mixing efficiency is therefore obtained by placing it in the centre of the torpedo. Excessive splashing prevented this on the model unless the gas rate was drastically reduced. Tests with a twin nozzled vertical lance, which projected the gas evolution areas within the body of the torpedo reduced the problem. This type of lance has been operated in practice in Japan but is prone to material flow problems and is only being slowly adopted by other operators. Many plants operate torpedoes with smaller length to diameter ratios than those at Appleby-Frodingham Works, and in these the use of a vertical lance is more feasible. The Appleby-Frodingham plant currently uses a lance angle of 70° to the horizontal. This is as close to the vertical as plant configuration and flexibility allow and the model results confirm its use.

[didn't test off centre

The skulls in the torpedoes are formed from a combination of blast furnace and desulphurisation slag and chilled metal. A skull has been known to limit the iron carrying capacity of a torpedo by 50%. The severity of skulling is presently limited by controlling the frequency of desulphurisation of individual torpedoes. This allows some of the skull to be eroded during casting and with the slag to be drained out with the iron on pouring or into slag pits, whilst preventing any further build up due to injection. The study of metal flow patterns when simulating a simple skull formation illustrated their significance in relation to desulphurisation performance. Any skull build up must be avoided if plant efficiency is to be maximised.

A major factor in skull formation was that the post desulphurisation slag, in particular the large rafts which occurred, were not removed from the torpedo either during pouring or attempted slag draining. Experiments with a torpedo model showed that slag removal during metal pouring was principally dependent on pouring rate, and that slag lump removal was considerably improved by using a rectangular rather than a rounded torpedo mouth. To obtain a good (closed) pouring stream the corners of the rectangular mouth had to be angled slightly. The mouth shape of several torpedoes at the Appleby-Frodingham Works was modified, and plant data indicated that a reduction in slag build up was obtained.

Unfortunately during operation the mouth corners were eroded and to maintain stream control the pouring rate was reduced with a consequent reduction in slag removal. To maintain the advantages of the larger mouth attention has to be paid to method of mouth construction and the refractory material used.

The problem of slag retention/skull formation should be reduced by fluxing the torpedo slag. The difficulty of mixing a flux with the slag in the Appleby-Frodingham torpedo precludes the simple use of bagged additions through the torpedo mouth. Soda ash injection with the carbide to flux the slag and attack the skull directly was partially successful. The quantity of soda ash added (10% of the mix) was insufficient to flux the slag but torpedo tare weight data did indicate a reduction in skull formation. This approach can only be used with a non-fuming flux or where a plant has suitable fume collection and cleaning facilities.

How much needed [illegible]

In order that the benefit of reduced iron sulphur content can be passed on to the steelmaking process it is essential that the post-desulphurisation slag is removed from the iron before it is charged to the steelmaking vessel. This is normally done by the use of a mechanical skimmer. The success of the method is limited by slag condition and the manoeuvrability of the skimming machine. A technique using gas bubbling to drive slag toward the skimmer had proved effective with slags from the Galag (magnesium) process.

Model work showed that it was also applicable to the larger quantities of granular slag produced by carbide injection. The use of gas to aid skimming produced an increase in the amount of slag which could be removed, and reduced the time required. It should be noted that when a fluid slag was simulated on the model, using oil, some break-off of oil droplets occurred, which then circulated in the water. This suggested that in practice, with a fluid slag, the benefits of the method might be reduced unless the gas flow was kept to a minimum.

PART TWO

DESULPHURISATION IN TRANSFER LADLES

11. NEW DESULPHURISATION PLANT DEVELOPMENTS

The results obtained from the model work and the other work on the project have given useful background data for a large capital development project in which the author has been involved. This was the provision of improved desulphurisation facilities at the Appleby-Frodingham plant.

At Appleby-Frodingham the torpedo injection plant was designed to treat up to 1.5 m.t.p.a. However it was soon evident that a high torpedo treatment frequency led to the rapid build up of skulls in the torpedoes. As has already been noted the presence of a skull severely decreases desulphurisation efficiency, producing more slag for any given final sulphur level which then augments the formation of skull. A reduced treatment level gave the opportunity for some of the skull to be 'washed' out by the iron during casting at the blast furnaces and pouring at the steelplant. In addition to this, because of changes in plant operation and raw materials it became necessary to lower the final sulphur level of the desulphurised iron. This in itself produced an increased slag load on the system. Therefore the plant capacity was reduced to 1 m.t.p.a.

Various solutions to the skulling problem were tried, in particular the addition of slag fluxing materials through the torpedo mouth at various stages in the torpedo filling to emptying process. None of these were successful because of the difficulty in obtaining good mixing between the slag in the torpedo with the additive, and because none of these could attack the skull itself. The use of soda ash (section 8.) as part of the desulphurising mixture did prove successful but could not be used as routine operation because of the fumes evolved.

A commonly reported solution to the slag build up problem is that of torpedo draining, in particular the operation at Dofasco, Canada. On a plant where considerable transport distances are involved this causes substantial organisation problems. The principal feature of a successful draining practice is that of torpedo shape. The more squat and barrel-like the torpedo the more likely is it that draining will work. The very large length to diameter ratio of the Appleby-Frodingham torpedoes made the practice difficult to operate successfully. [illegible]

It may seem that a simple answer could have been to increase the size of the torpedo fleet. This however was expensive and there were reasons outside the scope of this thesis why this should not be done. [illegible] with [illegible] Des

The objective for desulphurisation in the future was to be capable of treating, on peak demand, all the iron produced, 3.5 m.t.p.a. It was initially envisaged that this could be achieved by adding a second torpedo station. For the reasons outlined above this could not be done. A close study of the operational and performance capabilities of the alternative systems was undertaken, to select a process which could achieve the new aims. The basis of my involvement in this work was the literature survey and continuous monitoring of the 'state of the art' for this thesis. The major processes in industrial scale use considered were:

change at Parkin ??

1. Soda Ash Treatment
2. Magnesium Based Processes
3. Transfer Ladle Stirring - The K.R. Process
4. Transfer Ladle Injection - CaC_2 Processes
5. Steel Desulphurisation

The detailed comparison of these processes could not be reproduced here. A simplified desulphurising material cost comparison for iron desulphurisation is given in Table 35. This shows that for desulphurisation from 0.05%S down to 0.01%S only the magnesium dunking process could be excluded on materials cost grounds alone. Process selection was therefore dependent on capital cost, ease of system operation, plant availability, and known operating problems.

WHY

WHAT IS 1.5M COST ALLOWED

TABLE 35

DESULPHURISATION METHODS - MATERIALS CONSUMPTION

COST COMPARISON

Method	Materials Consumption kg/t. Desulphurisation 0.05% to 0.010%	Cost £/t iron
Soda Ash Injection	est. 8.29	0.63
	(at £76.4/t)	
Galag Dunking	1.00	1.30
	(at £1300/t)	
Magnesium Injection	est. 0.7	0.91
K.R. Process	4	0.68
(Ind. grade calcium carbide).	(at £170/t)	
Transfer Ladle Injection	5.5	0.88
(85% CaC_2, 15% $CaCO_3$)		

Soda Ash Treatment

The traditional method of adding soda ash to the ladle during filling was rejected because of its erratic performance and its inability to reach low sulphur levels, even by using the re-ladling technique. Although soda ash performance could be improved by injection, problems of refractory wear and fuming (a fume which is particularly difficult to handle) remained a major consideration. Efficient slag removal is essential to any desulphurisation process and the very fluid soda ash slags are difficult to remove.

Magnesium Treatments

The most common means of using magnesium was in the Galag (magnesium coke) dunking process. It could produce low final sulphur levels even from very low initial contents, with a high desulphurisation efficiency. However the treatment quantity was fixed and although multiple immersions or treatments were possible this lack of flexibility was a handicap when high iron throughputs were considered. Long treatment times mean high temperature losses which affected the economics of the B.O.S. process by reducing scrap melting capacity. At the time of the assessment the development of magnesium injection was in the early stages. However on the basis of the results available, although the processes were very efficient, on economic grounds they could not compete in the U.K. with carbide based treatments. This cost comparison has continued and the position has not changed.

only the last mentioned.

In addition, a much greater degree of injection control is required with magnesium than for the alternative carbide materials.

Transfer Ladle Stirring - K.R. Process

Of the many stirring processes in use the K.R. process of Nippon Steel had consistently produced the best performance figures. The process had the advantage over injection of a much lower capital cost. The process was studied in some detail. Data from the operating plants substantiated the reported efficiencies. However although the treatment times were reasonable, the overall cycle time was found to be up to 60 min. Operators also revealed that the plants availability, primarily due to the maintenance of stirrers, was a problem particularly at high metal throughputs.

Steel Desulphurisation

The processes for the desulphurisation of steel were only applicable to killed grades and therefore could not meet the overall works requirement; the bulk of production proposed was balanced and rimmed steel. NOT AT .01%S

Steel desulphurisation by injection of materials such as calcium silicide and carbide or by stirring under a reactive slag were finding increased application where low sulphur levels, less than 0.01%, needed to be guaranteed.

The Works aimed for product mix contained only a small proportion of these qualities, which could be met by careful B.O.S. charge selection, and therefore steel treatment was not necessary.

However the demand for lower sulphur contents was increasing and it was noted that such a system could be necessary in the future.

Transfer Ladle Injection - CaC_2 Process

The transfer ladle injection system had been observed in operation at Krupp's Rheinhausen Works. The process was able to meet both the desulphurisation and logistic requirements of the Appleby-Frodingham plant. It had the advantage of being a process, and a material, with which the operators and engineers were familiar. After a careful economic and metallurgical study and comparison with the alternatives, this process was selected.

The new plant has recently been commissioned. It consists of a twin ladle desulphurising unit with its own deslagging and fume extraction and cleaning equipment. Iron is poured from the torpedoes at the existing hot metal pouring stations. The ladle is then lifted by crane and placed on a transfer car, the crane is then free for other duties. The car moves the ladle into the desulphurisation and skimming station.

Each of the two units can desulphurise and skim independently, which will enable, if required, the total iron input to the plant to be treated.

12. SIMULATION OF HOT METAL MIXING IN A TRANSFER LADLE DURING INJECTION

12.1. Introduction

The technical decision to install a transfer ladle desulphurisation system was taken on the basis of the data available in the literature and from that collected during plant visits etc. As for the torpedo injection plant, the factors which could affect the process were known but had not been quantified. The transfer ladle injection process was therefore identified as a system where model simulation could increase our understanding of the process.

The ladle model used was that in which the slag skimming experiments had been carried out, Fig. 65. For the measurement of homogenisation times the model was set up with the pH meter and recorder, since the torpedo model work had demonstrated their reliability.

12.2. Model Similarity

The same considerations for applicability of similarity criteria apply here as were discussed in Sections 4.1. and 4.2. Therefore the same modelling criterion has been used, i.e. that the rate of energy supply per unit mass of liquid should be the same for the model and the plant.

12.3. Modelling Parameters

12.3.1. Plant Conditions

The first stage is to calculate the rate of energy supply to the metal.

The plant conditions assumed, in this example of the calculation, are:

Transport gas rate	1.0 m^3/min.
Desulphurising agent rate	100 kg/min.
Lance immersion depth	3.0 m.
Metal temperature	1350°C.
Lance diameter	0.0254 m.
Desulphurising agent ratio	85 CaC_2: 15 $CaCO_3$.

Considering the transport gas alone

The rate of supply of kinetic energy is

$$= \frac{1}{2} \rho \; QV^2 = \frac{1}{2} \rho \, Q \left(\frac{Q}{A}\right)^2$$

$$= 0.5 \times 5.2 \times 0.01667 \times \left(\frac{0.01667}{0.000506}\right)^2$$

= 47.04 watts

The rate of supply of potential energy is calculated as in 4.3.1.

$$= \Pi \; V_N \quad \ln \left(1 + \frac{\rho g h}{\Pi}\right) \qquad (4.7)$$

$$= 2.90 \times 10^5 \times 0.01667 \times \ln \left(1 + \frac{6400 \times 9.81 \times 3.0}{2.90 \times 10^5}\right)$$

= 2418 watts

and assuming that the gas reaches the metal temperature as it reaches the surface so that an average temperature can be taken, the actual rate of energy input by the carrier gas is $2418 \times \frac{948}{273} = 8397$ watts

Hence the effect of kinetic energy on the system is negligible

For the carbonate decomposition:

An overall feed rate of 100 kg/min. gives 0.25 kg/sec. of carbonate. Assuming 100 per cent decomposition at 825°C and that this occurs instantaneously at the lance exit, the rate of supply of energy from 0.225 m^3/sec. gas is

$$2.90 \times 10^5 \times 0.225 \times \ln\left(1 + \frac{6400 \times 9.81 \times 3.0}{2.90 \times 10^5}\right)$$

$= 32700$ watts. Higher than Turbido

12.3.2. Model Operating Values

The model linear scale is $1/20 = \frac{Lm}{Lp}$

For the rates of energy supply to be the same (Sect.4.3.2.) the model ratio is given by

$$\frac{\rho m}{\rho p} \times \left(\frac{Lm}{Lp}\right)^3 = \frac{1}{6.4} \times \left(\frac{1}{20}\right)^3$$

$$= 0.0000195$$

$$= 1/51200$$

Therefore the rate of energy supply to the model should be

1) For the carrier gas 0.164 watts

2) For the carbonate decomposition 0.638 watts

The required gas rate is, by substitution in equation 4.7.

$$= \frac{0.802}{101325 \times \ln\left(1 + \frac{1000 \times 9.81 \times 0.15}{101325}\right)}$$

$= 0.000549$ Nm^3/sec.

$= 0.0329$ Nm^3/min.

$= 32.9$ l/min.

12.3.3. Estimation of Homogenisation Times

The derivation of model/plant time conversion is given in sect. 4.3.3., similarly

$$\frac{tm}{tp} = \left(\frac{Lm}{Lp}\right)^{\frac{2}{3}} = \left(\frac{1}{20}\right)^{\frac{2}{3}} = 0.136$$

The mixing times measured on the model must be multiplied by 7.37 to give the plant value.

12.3.4. Model Lance Diameter

The model theory assumes a negligible contribution to the mixing force by the kinetic energy released at the lance exit. It has been assumed that this condition is satisfied if

Model K.E. $\leqslant$ 10% of Model P.E.

For the case of 100 kg/min. injected at a 3m. immersion depth the model gas flow is 32.9 l/min., the P.E. thus created is 0.8019w.

$\therefore$ for the model assumption

$$A^2 \geqslant \frac{\rho Q^3}{2 \times 0.1 \times P.E.}$$

$$\text{i.e.} \qquad \geqslant \left(\frac{1.251 \times 0.000548^3}{2 \times 0.0819}\right)^{\frac{1}{2}}$$

$$\text{i.e.} \quad A \qquad \geqslant 0.0000355 \text{ m}^2$$

$\therefore$ Minimum lance diameter is 0.67 cm.

The lance was selected to satisfy this condition.

12.3.5. Variation in Assumed Standard Values

The effects of changes in the assumed standard plant operating values on the model gas flow rate are shown in Table 36.

12.3.6. Limitations of the Modelling Technique

The two assumptions which are most likely to influence the interpretation of the model results are: 1. The calculation of gas temperature and its effect on the potential energy released by the gas on plant and 2. That the effect of model size relative to the actual can be neglected.

It is possible, using experimental data (ref. 69) to estimate the detachment temperature of a gas bubble from a lance from a knowledge of its residence time. However in reference 69 this requires extrapolation to reach gas flows of 11 m^3/hr, giving a bubble temperature of 1250^{o}K. Carrier gas flows during injection are normally about 45 m^3/hr to 60 m^3/hr., the bubbles therefore have a much shorter residence time at the lance exit and hence a shorter time for heating and expansion before detachment and work is done on the system. The gas produced by the carbonate about 150 m^3/hr will be evolved at the decomposition temperature and this has been taken into account in the calculations. It is therefore believed that the method of calculation used in this thesis provides a good approximation to the real situation.

The mixing process in the transfer ladle is influenced greatly by eddy diffusivity and for the plant and model a large range of eddy sizes exist. The minimum size is controlled by the liquid kinematic viscosities, which are similar for water and steel. The maximum size is determined by the size of the vessel, as a result, the distribution of eddy sizes for plant and model and hence the proportion of mixing energy held by each eddy size will be different. Mixing is primarily dependent on the smaller eddies, circulation on the larger. This effect of vessel size produces an error in all model work of this kind. However it will to some extent be a function of the energy input being modelled and its method of introduction, with respect to the turbulence produced.

The errors in water model work: in the assumptions which have to be made, the choice of modelling criteria, and the experiments themselves generally mean that the bare results are only guides to the actual situation. When, however, they can be supported by plant information from the full scale operation, the model results can be used with far greater confidence.

TABLE 36

EFFECT OF VARIATION IN OPERATING VALUES ON MODEL GAS RATE

Reagent Rate (kg/min)	Plant Lance Immersion (m)	Plant P.E. from Reagent (w)	Model P.E. from Reagent (w)	Model Gas Flow Carrier Gas l/min	Total Model Gas Flow
100	3.0	32655	0.6378	6.7	32.9
80		26124	0.5102	"	27.7
60		19593	0.3827	"	22.4
100	2.5	27587	0.5388	6.8	33.3
80		22069	0.4310	"	28.0
60		16552	0.3232	"	22.7
100	2.0	22488	0.4392	6.9	33.9
80		17990	0.3514	"	28.5
60		13492	0.2635	"	23.1
100	1.0	11960	0.2336	7.4	36.0
80		9568	0.1869	"	30.3
60		7176	0.1402	"	24.6

Plant Carrier Gas Rate = 0.01667 m^3/sec.

13. PRACTICAL WORK USING THE TRANSFER LADLE MODEL

13.1. Introduction

The design specification for the transfer ladle desulphurisation plant gave the following data for plant operation:

Lance immersion depth	3m.
CaD injection rate	100 kg/min.
CaD mix ratio	85 CaC_2 : 15 $CaCO_3$

These conditions were based on plant processing requirements and experience gained on other, though smaller, treatment units.

The experimental work using the model was designed to study the effects of changes to each of these process parameters on the time for melt homogenisation and to determine therefore the probable effects on process efficiency.

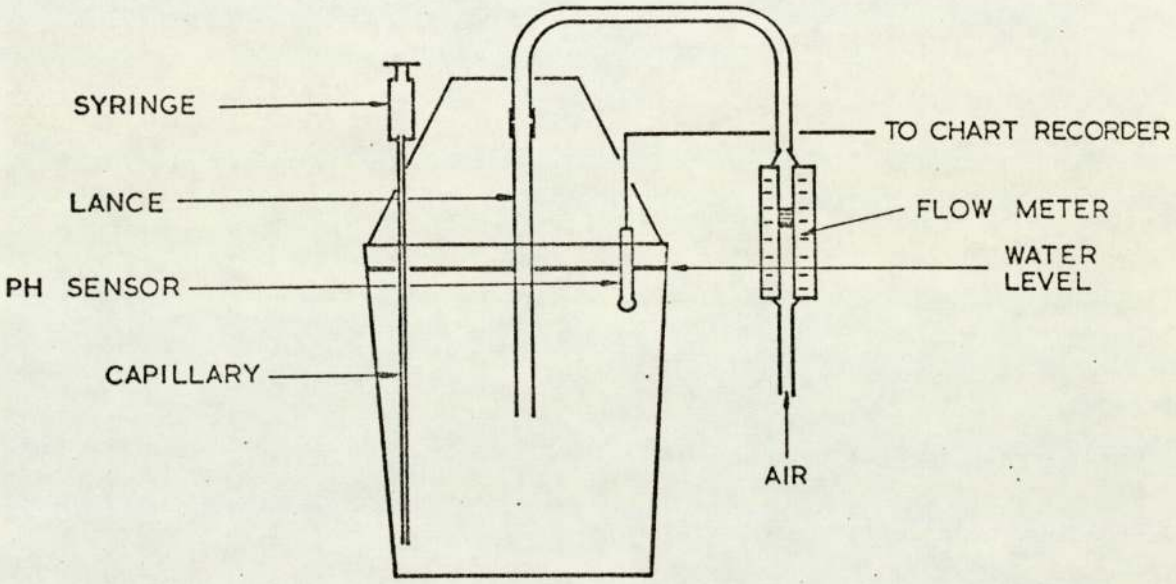
13.2. The Model

Set up as shown in Fig. 74. As for the torpedo experiments a pH meter connected to a single pen recorder was used to determine homogenisation time. To improve the reproducibility of the results, the technique was modified slightly:

1. the acid/alkali was added deep in the ladle, at a fixed position, by means of a syringe
2. since the 100% homogenisation point is approached exponentially and is therefore difficult to determine, a 90% value was taken in each case. Previous work, (ref. 70) outside this thesis has shown this to be a valid technique.

SCHEMATIC OF TRANSFER LADLE MODEL TEST RIG

FRONT ELEVATION



PLAN

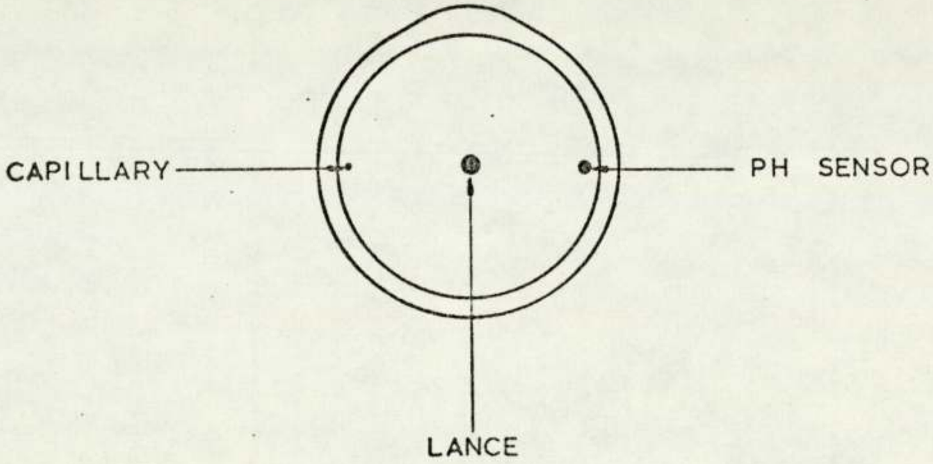


FIG. 74

The experiments were conducted for a range of lance immersion depths, injection rates, and $CaCO_3$ percentages, sufficient to produce a clear picture of the effects of each. The plant predictions for homogenisation time are given in Table 37.

13.3. Results

13.3.1. Variation of Lance Immersion Depth

The homogenisation time variation with lance immersion, for a range of $CaCO_3$ contents from 0 to 15, is given in Fig. 75. The zero level, i.e. for a carrier gas plus calcium carbide only, is included for completeness.

As the immersion is reduced from the normal operating level of 3m. to 2m., the mixing time increases relatively slowly by approximately 2 minutes. This rate of increase is common to each carbonate content examined. When the lance is withdrawn further the mixing time begins to increase rapidly, a 2 min. increment being obtained in 0.24 m.

13.3.2. Variation of $CaCO_3$ Content in the Desulphurising Mix

The homogenisation time variation with carbonate content for injection rates from 20 to 100 kg/min. is shown in Fig.76. The curves have the same shape as those in the previous section. At 100 kg/min. reducing the $CaCO_3$ content from 15% to approximately 11% has little effect on the mixing time; below 11% the time begins to increase rapidly.

TABLE 37

HOMOGENISATION TIME PREDICTIONS FROM MODEL RESULTS

Injection Rate kg/min	Immersion Depth m.	%$CaCO_3$ in mix	90% Homogenisation Time min.
100	3.0	0.0	13.3
		2.5	5.9
		5.0	3.6
		10.0	1.4
		15.0	0.8
	2.5	0.0	15.1
		2.5	6.6
		5.0	4.4
		10.0	2.0
		15.0	1.4
	2.0	0.0	20.2
		2.5	8.3
		5.0	6.2
		10.0	3.4
		15.0	2.8
	1.75	0.0	24.5
		2.5	11.0
		5.0	8.4
		10.0	6.3
		15.0	5.4
60	3.0	2.5	8.7
		5.0	5.7
		10.0	3.6
		15.0	1.6
	2.5	2.5	9.7
	2.0	2.5	13.3
		5.0	9.7
		10.0	7.1
	1.5	2.5	22.0
		5.0	18.2
		10.0	13.1

TABLE 37 (Cont'd)

Injection Rate kg/min	Immersion Depth m.	%$CaCO_3$ in mix	90% Homogenisation Time min.
80	3.0	2.5	6.4
		5.0	4.2
		10.0	1.8
		15.0	1.6
40		2.5	9.8
		5.0	7.4
		10.0	4.0
		15.0	2.7
20		5.0	10.8
		10.0	6.6

As the injection rate is decreased, i.e. as the energy input is decreased the reduction of % $CaCO_3$ becomes more significant. At zero % $CaCO_3$ the curves for each injection rate converge. It has been assumed that the carrier gas volume would not be significantly adjusted to accommodate the lower material flow rates. This is a feature of the type of injection equipment used on the plant, the carrier gas could be adjusted slightly but the principal control of injection rate is using the excess pressure in the dispenser and its outlet orifice size.

13.3.3. Variation of Injection Rate

Time variation with injection rate is shown in Fig. 77. Again the curves exhibit the same characteristic shape. At the high carbonate content used on plant (15%), the mixing time is barely reduced by a fall in injection rate from 100 to 70 kg/min. However for lower carbonate contents and/or injection rates the increase in mixing time is more rapid.

13.4. Discussion

Examination of Figs. 75 to 77 would suggest that the desulphurising ability of the plant would be maximised by the following operating conditions:-

1. Lance immersion depth, greater than 2.5 m.
2. %$CaCO_3$ in the mixture, greater than 12.5% (possibly 10%).
3. Injection rate, greater than or equal to 70 kg/min.

These parameters are met by both the plant design and current operating conditions. The plant design figures have been used as the basis for this work and were used consistently during the commissioning of the plant itself.

Although the modelling did not attempt to simulate the condition of the metal surface splashing, it did indicate that the injection rate of 100 kg/min. was high given that the other parameters were unchanged. In practice this has proved to be the case and the rate was decreased to 80 kg/min. Work at the Krupp plant also operating the transfer ladle system had suggested that lance immersion could be reduced from 3 m. without detriment to the plants performance. The benefits are a reduction in lance length, and hence cost, and/or a reduction in skulling problems on the non refractory section of the lance, (this should have a service life far greater than the immersed section). For a short period the lance immersion depth was reduced to 2 m, the quantity of desulphurant injected remained unchanged at that established for the original practice. The modification caused no problems for the high final sulphur levels aimed for, 0.01% and 0.02%, which are required for normal steel qualities. However for the low sulphur aims, 0.005% maximum, the previously predicted carbide quantities were no longer sufficient. The lance immersion was therefore increased to 2.75 m. which is well into the area predicted by the model for maintaining high mixing efficiency. DID IT WORK

RESULTS

PREDICTED HOMOGENISATION TIME -VARIABLE LANCE IMMERSION

INJECTION RATE 100 kg/min.

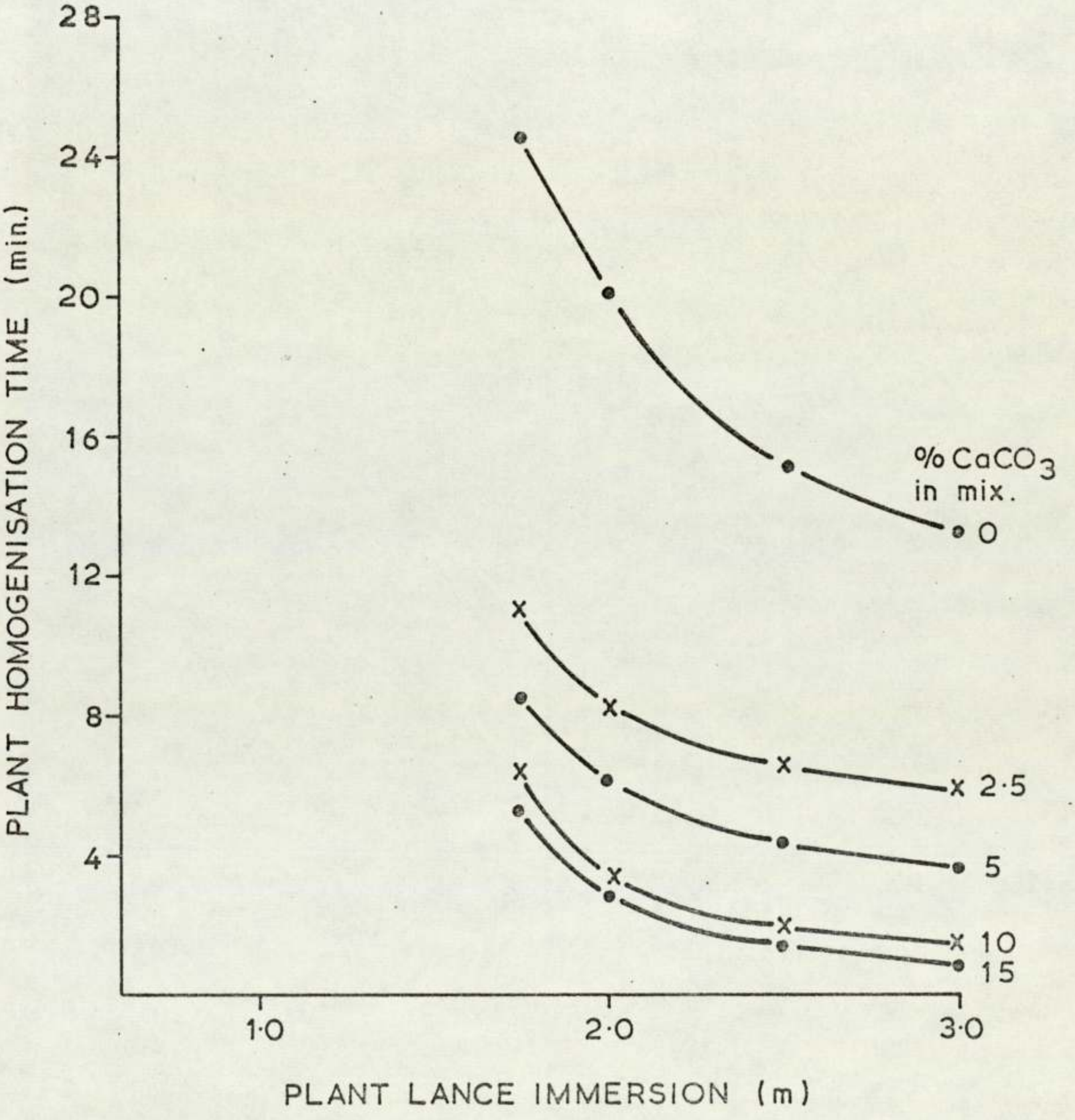


FIG. 75

PREDICTED HOMOGENISATION TIME

- VARIABLE % $CaCO_3$ IN MIX

(LANCE IMMERSION DEPTH 3·0 m.)

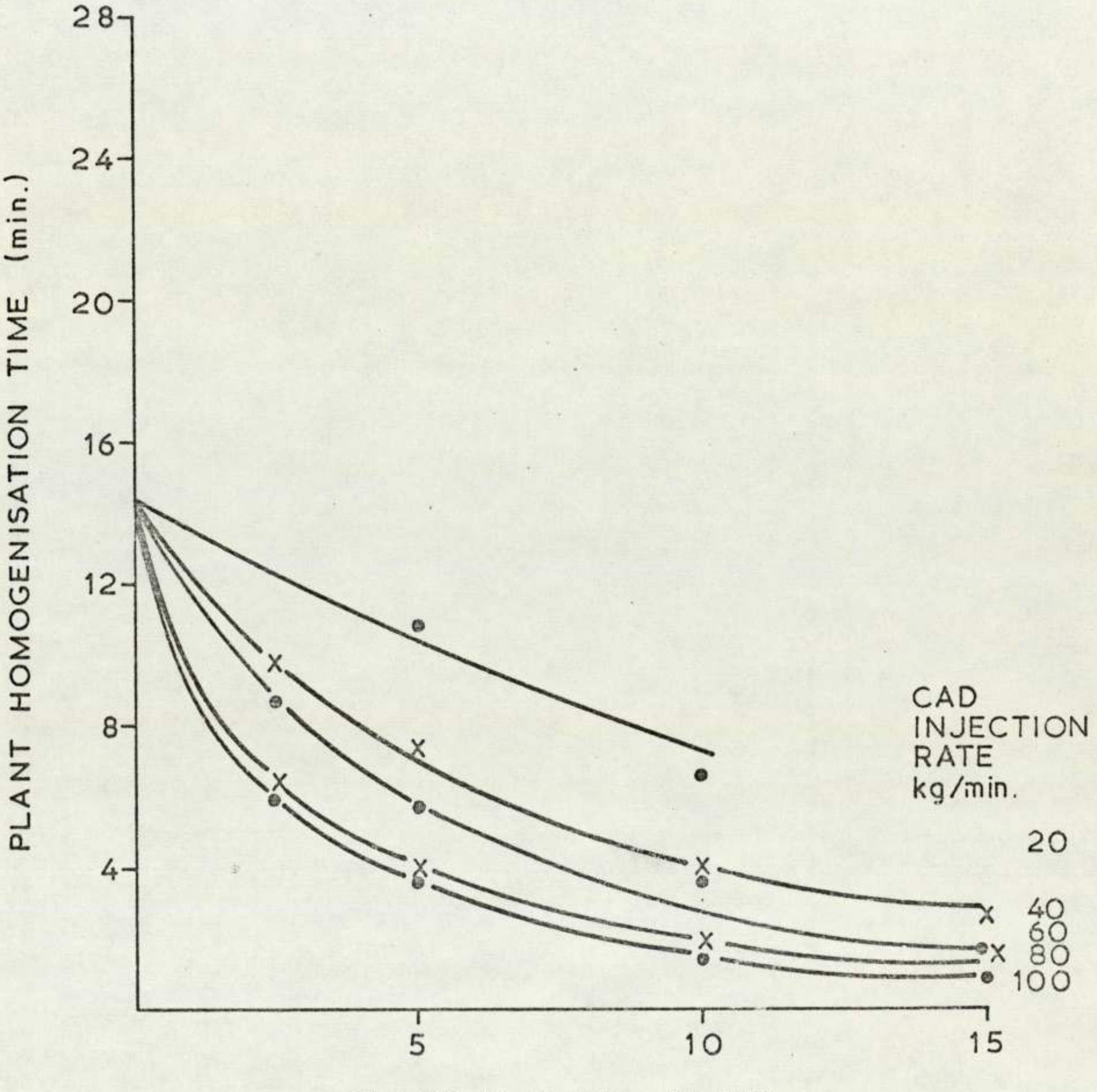


FIG. 76

PREDICTED HOMOGENISED TIMES – VARIABLE INJECTION RATE

(LANCE IMMERSION DEPTH 3·0 m.)

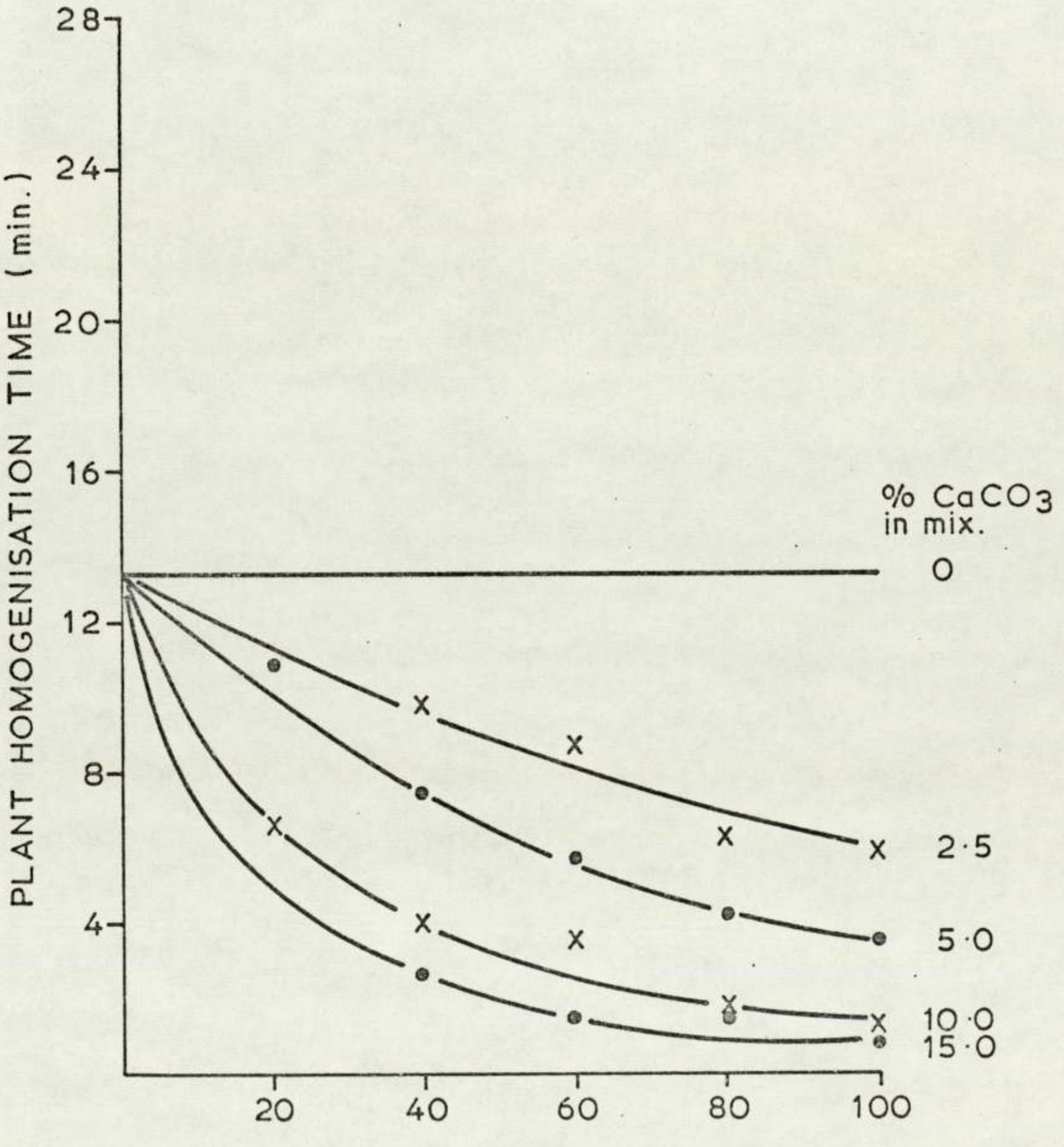


FIG. 77

The graphs Figs. 75 to 77, clearly show the general relationship between the operating variables. However it was difficult to use them to draw direct comparisons. To facilitate this, an equation was developed, (ref. 71), to predict homogenisation time

$$\frac{1}{\sqrt{t}} = -0.031 + 0.176 \sqrt{h} + 6.18 \times 10^{-5} \times R \times \%CaCO_3 \times h^2 \quad (12.1)$$

where t = time in min.

h = immersion depth, m.

R = injection rate, kg/min.

Using this equation to calculate time, a sensitivity analysis was carried out for the other variables. The results are given in Table 38, and Fig. 78. On a percentage change basis injection rate and $\%CaCO_3$ have the same effect on mixing time. The time is the most sensitive to lance immersion depth.

On the desulphurisation plant lance immersion is closely controlled but by reference to a fixed point and not to metal level in the ladle. It will therefore vary as the metal weight is adjusted to meet heat balance requirements and as the ladle wears. Considering the former condition only, variations of + 15 t. to - 20 t. are normal. The carbonate composition is controlled by the supplier and is regularly checked; it does not normally vary more than ± 3% from the aim. The injection rate can vary during or between treatments for fixed injector operating conditions. A change in lance back pressure due to variable immersion or partial blockage is the most common reason. The normal range of flow is ± 10 kg/min. from the aim. These expected ranges are also shown on Fig. 78.

TABLE 38

SENSITIVITY ANALYSIS DATA FOR PLANT HOMOGENISATION TIME

% Change from Standard	Immersion Depth h, (m)	Injection Rate R, (kg/min)	%$CaCO_3$	Homogenisation Time t, min.
0	3.0	100	15	0.814
+10	3.0	100	16.5	0.704
+20			18.0	0.615
-10			13.5	0.952
-20			12.0	1.129
+10	3.0	110	15	0.704
+20		120		0.615
-10		90		0.952
-20		80		1.129
+10	3.3	100	15	0.593
+20	3.6			0.442
-10	2.7			1.146
-20	2.4			1.662

$$\frac{1}{\sqrt{t}} = -0.031 + 0.176\sqrt{h} + 6.18 \times 10^{-5} \times \%\,CaCO_3 \times R \times h^2$$

SENSITIVITY OF HOMOGENISATION TIME TO CHANGES FROM STANDARD OPERATION

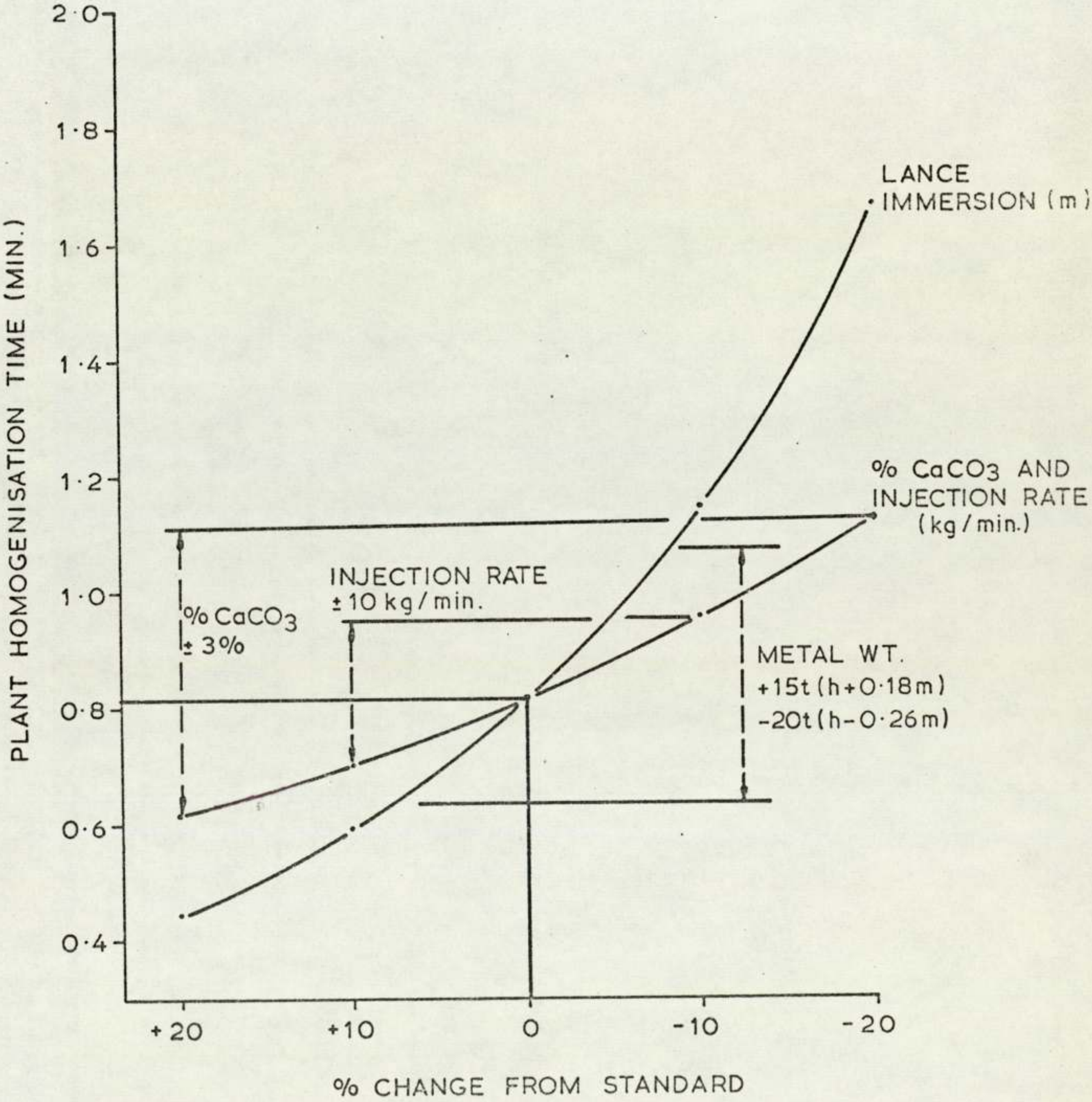


FIG. 78

The effects of metal weight and $CaCO_3$ content are almost equal and double the injection rate effect.

The maximum favourable and unfavourable changes given above have been used to calculate the homogenisation times for the best and worst cases as normally encountered, these are 0.43 min. and 0.76 max. respectively, a difference of 19.8 secs.

TABLE 39

EFFECT ON HOMOGENISATION TIME OF FAVOURABLE & UNFAVOURABLE CHANGES IN PLANT VARIABLES

	h	$\%CaCO_3$	R	t
Best Case	3.18	18	110	0.433
Worst Case	2.74	12	90	0.761

This short time is not likely to be significant during normal operations where the final concentration of S is relatively high, 0.010% and 0.020% are common aim levels. It may however become important when low final %S levels are required, say 0.005% max.

WHAT WILL IT BE
you JUST
DROPPED LANCE
Page 226

14. DISCUSSION

14.1. TRANSFER LADLE DESULPHURISATION

Work carried out for the steelplant and the rolling mills had shown that considerable financial savings could be obtained by an overall reduction in the steel sulphur level produced. This coupled with the very strong market demands for lower sulphur levels meant that the works had to increase its desulphurisation capacity to over 80% of the hot metal produced. The difficulties of expanding the torpedo operation in the context of Appleby-Frodingham conditions were obvious, and the transfer ladle injection system was selected as the best means of achieving the desired result.

The modelling technique which had been applied to the torpedo plant was equally valid for the new equipment and experiments were devised to examine the major variables of this process. These are the lance immersion depth, the material injection rate and the %$CaCO_3$ in the desulphurant. The effect of lance position across the ladle diameter had been the subject of study in model work related to the gas flushing of metal, ref. 70). This had shown that this ceased to be an important factor, with respect to mixing, at high gas rates such as those encountered during desulphurisation.

The predictions for mixing time made from the model results showed that for each variable studied, the value at which the plant operates will produce mixing conditions in the iron giving maximum aid to the desulphurisation reaction. As a result of splashing problems the injection rate used during plant commissioning was reduced from 100 kg/min. to 80 kg/min. The model confirmed that this shift should not be detrimental to carbide consumption for a given sulphur removal. However, further decreases, to less than 70 kg/min. should be avoided.

As has been stated, the function of the carbonate is to promote mixing. However it also reduces the desulphurant cost, there are therefore benefits in increasing its content. Because of the splashing problem, as the carbonate is increased the injection rate must be reduced. The relationship between these two factors and the mixing time is such that a reduction could be made from 80 kg/min. at 15% to 60 kg/min. at 20% without substantially affecting the time, further reductions however do have a marked effect. The transfer ladle process is characterised by very short mixing times and it is probable that at the lower injection rates the process becomes limited by the rate of supply of calcium to the system and therefore process efficiency may decrease. The other important factor is the total time available for the process and its time related iron temperature losses in the context of B.O.S. shop operation and economics. Increasing the carbonate level must therefore be the subject of careful plant evaluation.

RESULTS??

HOW DO YOU KNOW

CALCULATE TEMP LOSS

A sensitivity analysis relating changes in the variables to predicted mixing times showed that given the present operating values any normal changes which occur on a day-to-day or ladle-to-ladle basis should not affect process efficiency.

14.2. GENERAL DISCUSSION

In recent years there has been a steady growth in demand for better quality steel; in most cases this has meant continued reductions in the steel sulphur level. At the same time there have been major changes in the economics of iron and steel manufacture. Together, these have directed much effort into obtaining the lowest cost route to low sulphur steel.

The basic oxygen process is not an efficient desulphuriser and to produce the low levels of sulphur required the sulphur input to the steelmaking vessel has to be limited. Although the ironmaking process is efficient at sulphur removal, especially to moderate iron sulphur levels (c. 0.040%), the size of the steelmaking sulphur load from other sources, for example, scrap, makes it uneconomic to obtain low sulphur steel solely by the production of very low sulphur iron. The need for some intermediate process is therefore obvious.

The early methods of external desulphurisation using soda ash were deficient in several respects, e.g. unreliability of end points and excessive fuming. Attempts to overcome these difficulties by varying the method of addition and combining the soda with other materials, in particular lime, were relatively successful. However these lime based reagents required high material consumptions to produce the desired result.

This took time and produced large slag loads which were difficult to handle. It was soon realised that more reactive materials such as calcium carbide, and calcium cyanamide better satisfied the requirements for an intermediate desulphurisation process.

It had always been recognised that desulphurisation efficiency was increased by improving the contact area and time between the reagent and the high sulphur iron. Early work showed significant improvements in efficiency by using fine rather than coarse industrial grade materials. Much of this development work was carried out in cylindrical iron transfer ladles. These factors led to the early use of mechanical stirring systems to thoroughly mix the iron and reagent. Stirring systems are in use today on units ranging up to 300 t., but in general are applied to the low throughput production of very low sulphur iron. The main difficulty with the plants is availability. In the larger units the stirrer is immersed deep into the metal and rotated at high speed. This practice differs from that at the smaller plants, but is explained simply by the relative scale of the operations. The initial slow development of injection systems grew with the expanding use of torpedo ladles for iron transport. For these ladles injection provided the best means of combined addition and stirring. However, the quantity of gas used to optimally transport and inject the desulphurant was insufficient to give good stirring of the iron and hence a good desulphurisation efficiency. The obvious solution, to increase the transport gas rate, has been used, but there are difficulties with material entrainment in the gas which reduce the reaction efficiency.

The now almost universally adopted technique is to mix the desulphurant with a gas evolving agent.

The first major step taken at the Appleby-Frodingham Works to satisfy the lower sulphur steel demand was to install a 1.5 m.t.p.a. capacity torpedo desulphurisation plant, in 1973, as part of the massive Anchor development. The plant injected a 70 : 30 mixture of calcium carbide and calcium carbonate. In terms of desulphurisation performance, given good operating conditions, this plant proved the equal of any in the world. However, the process, because of the slag volume and type created, gave considerable operating problems. Desulphurisation capacity was increased to 3.5 m.t.p.a. in 1979 by the installation of a transfer ladle injection plant. The same desulphurant was used but the carbonate content was reduced to 15%.

The understanding of the torpedo injection process and the problems of slag removal were increased significantly by water model experiments in conjunction with plant trial data. The results helped in the decision making processes necessary to maximise the plants efficiency. The water modelling technique was also applied to the transfer ladle injection system. This plant is only recently fully commissioned. However, some of the effects indicated by the model have already been reproduced in practice.

At the torpedo treatment plant, in order to maximise the efficiency of desulphurisation (as measured by the carbide consumption) the injection rate was reduced to 60 kg/min. It is of particular interest therefore to compare the model results for that situation with those of the transfer ladle system.

For the torpedo ladle the homogenisation time varied considerably along its length, (see Table 18). The predicted times varied from 1.9 min. immediately adjacent to the lance, to 4 min. at the torpedo end furthest from the lance exit. These results and the experience of plant operation showed the importance in this system of maximising the mixing energy input in conjunction with the limited time available for the carbide to react with the sulphur in the metal.

In contrast the predicted times for the transfer ladle are much shorter, Table 37, and furthermore represent the whole bulk of the metal. The transfer ladle operation removes the dangers of dead zone formation and the disastrous effects of internal skulling observed in torpedoes.

In the transfer ladle process, the mixing energy introduced is more fully utilised than for the torpedoes. With respect to desulphurisation performance, this places the emphasis on the chemistry of the process rather than its physical characteristics.

Carbide is highly reactive with sulphur but its major limitation in iron is that desulphurisation remains a solid liquid reaction. In an attempt to improve this situation production trials have taken place in Germany with a "eutectic calcium carbide". It is suggested that its lower melting point enables a liquid-liquid reaction to take place. As yet this work is not published and further comment cannot be made. If a large reaction efficiency improvement was required the obvious choice of desulphurant is magnesium. This is growing in use as an injectant, however its high cost inhibits its use at most European plants.

15. CONCLUSIONS

15.1. Torpedo Desulphurisation

15.1.1.

1. The rate of addition of the desulphurising agent used at Appleby-Frodingham Works (60-80 kg/min) produces mixing of all the metal in the torpedo.
2. As the rate of addition decreases mixing efficiency is reduced. 50 kg/min. is thought to be a practical lower limit.
3. Torpedo internal skulling seriously reduces the efficiency of the desulphurising process.
4. For maximum efficiency the injection lance should be immersed to the maximum depth possible.
5. Mixing of the iron is maximised at low reagent rates by placing the lance exit at the centre of the torpedo.
6. Central (vertical) lancing is not possible with the present torpedo design because of excessive splashing.
7. Nozzles fitted to vertical lances reduce the splashing problem.
8. The present angle of insertion of the lance, 70°, avoids excessive splash except on very full torpedoes and is probably as close to vertical (90°) as can be tolerated under plant conditions.
9. The best estimate of torpedo iron sulphur level is obtained by multiple sampling from the blast furnace runner during casting. The samples should be taken at intervals corresponding to equal weights of metal cast.

10. No significant change in iron analysis occurs between the blast furnaces and the desulphurisation plant.

11. The routine runner analysis is not sufficiently accurate to use as a starting point for desulphurisation.

12. For routine and trial applications a pre-treatment iron sample taken at the desulphurisation plant should be used.

13. The sampling unit developed, successfully takes samples simultaneously at different metal depths.

14. No evidence of iron stratification in the torpedo was found from the trials.

15. Stratification could occur if the furnace casting rate was low or a large change in iron analysis took place during the topping-up of a fairly full torpedo.

16. For desulphurisation by injection of calcium carbide into torpedo ladles, it is necessary to add a gas evolving agent to stir the iron.

17. The most common gas evolving agent is calcium carbonate.

15.1.2. Torpedo Mouth Design

1. The design of a torpedo mouth has a significant effect on the ability of the torpedo to drain retained slag.

2. The rate of rotation of a torpedo is the principal factor controlling the degree of slag removal during hot metal pouring. The faster the metal is poured the more slag is removed.

3. Torpedo desulphurisation produces large rafts of slag. These are most easily removed if the width of the torpedo mouth is large.

4. A rectangular torpedo mouth enables the maximum slag removal.
5. In order to obtain a controlled metal stream from a rectangular mouth the edges of the mouth must be angled.

15.1.3. Torpedo Skull Removal and Slag Treatment Using Soda Ash

1. A 10% addition of soda ash with the desulphuriser was insufficient to modify the slag and hence its pouring characteristics.
2. Soda ash treatment during the tests performed appeared to reduce skull formation. However the limited trial duration prevented verification.
3. Soda ash injection is only practicable on plant which has good fume collection and cleaning facilities.
4. The problems of dispensing and conveying soda ash in an injection system can be overcome by careful selection of the material and equipment used.

15.2. Transfer Ladle Desulphurisation

15.2.1.

1. At the Appleby-Frodingham plant both the design and current operating conditions maximise the mixing of iron in the ladle.
2. Mixing is maximised by a lance immersion greater than 2.5 m; by a percentage of calcium carbonate in the mix greater than 12.5%, by an injection rate greater than 70 kg/min.
3. The time for homogenisation may be predicted by equation 12.1

$$t^{-0.5} = -0.031 + 0.176\ h^{0.5} + 6.18 \times 10^{-5} \times R \times \%\ CaCO_3 \times h^2$$

4. Homogenisation time is most sensitive to the lance immersion depth.
5. Given the normal variation in the parameters examined the maximum difference in homogenisation time between treatments should be 19.8 secs.
6. The variables examined do change during routine plant operation. If the most unfavourable combination is encountered the limiting values given in 2) above are not exceeded.
7. Under the mixing conditions which prevail in the transfer ladle process, desulphurisation performance can only be improved by increasing the residence time of the calcium carbide within the iron or by using a more reactive reagent such as a low melting point carbide or magnesium which vaporises.
8. For desulphurisation by calcium carbide injection into a transfer ladle it is necessary to add a gas evolving agent to stir the iron.
9. The proportion of gas evolving agent in the mixture is limited by the surface turbulence produced at the injection rate being used. However the model has shown that high levels will not significantly affect the metal mixing time.

15.2.2. Transfer Ladle Slag Removal

1. For iron desulphurisation to benefit the steelmaking process efficient slag removal is essential.
2. The use of gas bubbling at the back of the ladle during skimming increases the amount of slag which can be removed and reduces the process time.
3. The increase in slag removal obtained using gas is dependent on the gas flow rate applied.
4. High rates of gas during skimming drive the slag into areas from which it can be removed.
5. The process is less dependent on the position/depth at which the gas is introduced than on the gas flow rate.
6. The benefits shown for desulphurisation slag could not be demonstrated as easily for blast furnace slag because of difficulties with its simulation on the model. However the process has been observed in plant use with this slag.

16. SUGGESTIONS FOR FURTHER WORK

1. During the injection process the interaction of the injected particles with the carrier gas is not well understood, especially where decomposition of all, or a proportion, of the particles occurs. A study of the phenomena involved could benefit plant operation.

2. It is claimed that the chemical efficiency of the transfer ladle injection process can be increased by the use of multi-nozzle injection lances. This should be examined with respect to the mixing time obtained, and in terms of the carrier gas/particle interactions.

17. NOMENCLATURE

	Units (if not specified)	Symbol
Mass	kg	M
Velocity	m/sec	V
Viscosity		μ
Density	kg/m^3	ρ
Length	m	L
Gravity (Const.)		g
Surface tension	N/m	σ
Model Scale		Subscript m
Plant Scale		Subscript p
Volumetric Flow rate	m^3/sec	Q
Area	m^2	A
Total Pressure	N/m^2	π
Volume	m^3	V
Pressure	N/m^2	P
Normal temp. & Pressure		Subscript N
Energy	Nm	U
Time	Sec	t
Specific Heat	J/kg^oK	C
Temperature	^oK	T
Thermal conductivity		K

18.

APPENDIX 1

Assessment of Desulphurisation Efficiency

Throughout Europe, the traditional means of assessing desulphurisation performance has been by the calculation of an efficiency factor, α :

$$\alpha = \frac{\text{kg Reagent}}{\text{tonnes metal} \times \Delta\,\%S \times 10^3}$$

low α values indicate high efficiency. α has been used by the Scunthorpe Works, quality control department for routine performance monitoring.

It is however highly dependent on the initial sulphur level of the iron being treated, and only loses this dependence at initial values greater than 0.07%S (in the case of torpedo treatments). At initial levels less than this, α increases exponentially as the sulphur content decreases. Its use should therefore be limited to those plants where the initial level is relatively constant.

Ideally any measure of plant efficiency should be independent of initial sulphur level. It has been suggested that this condition is satisfied by K where

WHY

WHEN So in equation.

$$K = \frac{\ln \frac{S_o}{S_F}}{M} \qquad \left\{ \text{from } S_F = S_0\, e^{-KM} \right\}$$

What's Second equation

where S_O and S_F are the initial and final sulphur levels and M is the reagent consumption, kg/t. hot metal, (ref. 72). The K factor has been adopted by a number of plants. However, when examined for application at the Appleby-Frodingham Works, although it proved to be relatively independent of initial sulphur level the range of values obtained (0.15 to 0.50) was such that no benefit could be seen in changing from the α value method.

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