

# The sampling of liquid hot metal and steel at a steelplant

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## SYNOPSIS

The investigation, which was conducted at Iscor's Newcastle works (in Natal), was aimed at the development of reliable, consistent, and cost-effective methods of sampling.

In the sampling of hot metal, it was found that lollipop and spoon samples had identical sulphur analyses, and negligibly different silicon analyses. Thus, spoon sampling of the hot metal was implemented, with a resultant saving of over R100 000 per annum on lollipop samplers.

In the sampling of steel, aluminium-killed samples were found to have lower phosphorus analyses than titanium-killed samples. Spoon sampling was rejected in this application since the use of titanium wire would be too costly.

It was decided that titanium would be used as the deoxidant in lollipop samples of steel, and that the Leco carbon/sulphur analyser would be used as the sole arbiter of sulphur content.

## SAMEVATTING

Die ondersoek wat by die Yskor-werke in Newcastle (Natal) ingestel is, was gemik op die ontwikkeling van betroubare, bestendige en koste-effektiewe monsternemingsmetodes.

By die monsterneming van warm metaal is daar gevind dat 'suiglekker-' en lepelmonsters identiese swawelontledings gegee het met 'n onbeduidende verskil in die silikonontledings. Daar is dus lepelmonsterneming van die warm metaal toegepas, met 'n gevolglike besparing van meer as R100 000 per jaar ten opsigte van 'suiglekker'-monsternemers.

By die monsterneming van staal is daar gevind dat aluminiumgetemde monsters laer fosforontledings as titaangetemde monsters gehad het. Lepelmonsterneming is vir dié doel afgekeur omdat die gebruik van titaandraad te duur sal wees.

Daar is besluit om titaan as die deoksiderder in 'suiglekker'-staalmonsters te gebruik en dat die Leco-koolstof/swawelontleder as die enigste arbiter wat betref die swawelinhoud gebruik sal word.

## Introduction

The sampling of hot metal and steel is of paramount importance in the production flow of a steelworks because the successful treatment of the liquid metal depends largely on the correct analysis of representative samples.

From the commissioning of Iscor's Newcastle works in 1974, a fair number of problems were encountered in the sampling of hot metal at the desulphurization station as it arrived from the blast furnaces, and again when it was about to be charged into the basic oxygen furnaces (B.O.F.) Further problems were experienced when samples of liquid steel were taken from the furnaces at the end point.

This paper describes the investigations carried out at Iscor that resulted in the development of reliable, consistent, and cost-effective sampling procedures.

## Hot Metal

The flow of hot metal and the sampling points at the steelplant are as follows. The liquid metal arrives at the desulphurization station from the blast furnaces in torpedo ladles. If the sulphur analysis at the blast furnaces is above 0,08 per cent, the metal is desulphurized by the injection of calcium carbide into the torpedo with the aim of lowering the sulphur content to about 0,08 per cent. The metal is then sampled, and the torpedo is sent to the hot-metal control, where it is poured from the

torpedo into a transfer ladle. During the pouring operation, soda ash is added to the ladle to lower the sulphur content to a predetermined level, which is set according to the quality of steel to be made.

However, if the sulphur analysis is 0,08 per cent or less, the metal is sampled only on arrival at the desulphurization station and no calcium carbide is added. Instead, the torpedo is transferred straight to the hot-metal control, where the desulphurization is conducted with soda ash according to the sulphur analysis at the desulphurization station.

The transfer ladle containing the hot metal is then transported from the hot-metal control pouring pit to the deslagging station, where the mixture of blast-furnace and desulphurization slag appearing on the top of the hot metal is skimmed off. This is done so that the sulphur does not re-enter the steel during the blowing of the B.O.F. A sample is taken from the transfer ladle so that the blowing and flux patterns can be determined, and the hot metal is charged into the furnace.

All the samples of hot metal from the normal production flow are analysed by spectrometers at the production laboratory. Sulphur is determined by Leco carbon/sulphur analyser only if a sulphur result is disputed.

In the sampling of a hot-metal bath, two methods can be employed: the use of dip samplers, commonly known as 'lollipops', or of a simple spoon from which the liquid metal is poured into a steel mould, where it solidifies.

The continuous problems that were experienced with lollipop-type samplers were associated with the occasional low temperature, and hence high viscosity, of the hot metal. This caused either the metal to chill in the quartz tube before it entered the steel pressing mould, or the

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mould to become only half filled. Further defects such as cracks and slag inclusions commonly occurred in lollipop samples. As a result, the success rate of the sampler was fairly low; occasionally, during the periods of low hot-metal temperatures, less than 40 per cent of the samples taken were satisfactory, making this type of sampling a very costly practice.

The objection raised against spoon sampling was that the sample was not representative of the whole bulk of hot metal because of suspected stratification in the torpedo ladle. The stratification was thought to occur particularly after the desulphurization treatment; it was assumed that the top of the hot metal from which the spoon sample would be taken was a reaction zone and that the sulphur analysis would be too low or inconsistent. It was claimed that a lollipop sample originated from a deeper level in the melt and was therefore more representative. In addition, it was considered that the pouring of the metal from the spoon into the mould resulted in the oxidation of silicon and carbon, and the analysis of such a sample would be incorrect, for example, for use in the calculations of the B.O.F. heat balance.

To establish the differences between the two sampling methods, an extensive trial programme was conducted at the desulphurization station.

The torpedo ladles were sampled by spoon and lollipop, and sampling continued until ten perfectly sound samples had been obtained by each method from the same torpedo both before and after desulphurization. An adequate number of torpedoes was sampled. The lollipops used had been obtained from a South African supplier, and were being used at the desulphurization station during normal production.

The sampling spoon used in the tests had a long stem and was always dipped into a gun-aid bath (B.O.F. gunning material) before being immersed in the metal. The liquid metal was poured from the spoon into a split steel mould resting on a copper plate, which was actually an old continuous bloom-caster mould plate connected to a water-cooling system that circulated chilled water inside the plate. This was done to increase the chilling effect of the copper, and hence to increase the thickness of the surface layer (consisting of white iron), the aim being to obtain samples that were as white as possible.

Trials were later carried out at the deslagging station in exactly the same way, i.e. ten spoon samples and ten lollipop samples from the same ladle.

All the samples were analysed twice by X-ray-fluorescence spectrometry, thus ensuring reliable average values.

### Steel

At the steelplant, steel is sampled at the end point of the furnace blow and, in the case of a reblow, after each reblow. Further samples are taken from the transfer ladles before the steel is sent to the continuous casting machines.

In principle, the same sampling procedures, i.e. spoon and lollipop sampling, were possible. The main problems encountered with the steel samples were pinholes due to inadequate deoxidation and slag inclusions on the sur-

face of the sample. Occasionally, the success rate of the sampling was poor.

It was felt that the first matter to be investigated was whether it was practically possible for spoon sampling to be used for end-point control. The trial was carried out by the taking of ten aluminium-killed spoon samples and ten titanium-killed lollipop samples from the same heat. The spoon sample was taken from the furnace, and the aluminium wire was fed into the spoon. Then the sample was poured from the spoon into a tapered mould, where it was allowed to solidify for a short period. In the laboratory, a 2 cm high disc was cut from the bottom of the sample, and the cut surface of the disc was analysed by sparking the outer edge. In total, ten heats were sampled, and the samples were analysed on two different emission spectrometers, two X-ray-fluorescence spectrometers, and a Leco carbon/sulphur analyser.

The second step in the investigation was aimed at the finding of a suitable element for deoxidation that would, among other things, not bias the spectrometer analysis. The following three elements were tried: aluminium, zirconium, and titanium. In the trials, seven lollipop samples were taken with each of the three deoxidants from the same heat at the end point, a total of ten heats being sampled. The samples were analysed as before.

Thirdly, comparative trials were carried out to show the best lollipop sampler on the market for Iscor's conditions. Each of the four suppliers in South Africa at that time was asked to send a trial batch of fifty samplers for use with titanium as deoxidant. The main emphasis of this investigation was on the analyses obtainable on the samples from each type of sampler, the consistency (i.e. the magnitude of the standard deviation of the samples), the success rate, and the price. The samplers were compared by the taking of five samples of each type from the same heat. Ten different heats were sampled, and the samples were analysed as before.

The within-sample segregation effects in both the hot-metal and the steel samples were investigated by the grinding of several samples of varying chemical compositions in 1 mm intervals through the sample and sparking it after each grind. The difference through the samples was found to be within the limits of accuracy of the analysers, and no further attention was paid to this aspect in the trials.

## Results

### *Hot Metal*

The results for the spoon and lollipop analyses before and after desulphurization and at the deslagging station are presented in Figs. 1, 2, and 3 respectively. At the desulphurization station, only the sulphur analyses were considered, but at the deslagging station, the analyses of the other main four elements were considered as well as the sulphur analyses.

Fig. 1 presents the sulphur results for five typical heats where the samples were taken before desulphurization. There were small differences in the analyses before the desulphurization, but they are clearly distributed randomly: on three occasions the analyses were practically the same, and on two occasions the lollipop analyses were lower.

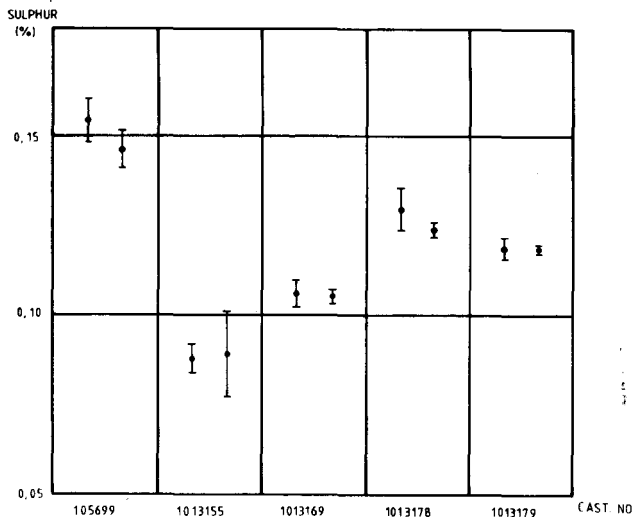


Fig. 1—Average sulphur analyses, with their standard deviations, for spoon and lollipop samples taken from the hot metal before desulphurization. In each column, the lefthand analysis represents the spoon samples, and the righthand analysis the lollipop samples

Five typical sulphur results from the heats sampled after desulphurization are shown in Fig. 2. It is quite clear that neither sampling system gives consistently lower or consistently higher sulphur analyses; the same random distribution applies as before the desulphurization. On two occasions, the sulphur values of the spoon samples were higher, and on three occasions they were lower.

With regard to the oxidation of silicon or carbon during pouring from the spoon to the mould, or to the difference in the analyses for the other elements at the deslagging station, the results show that there is no difference in the values for carbon, sulphur, phosphorus, or manganese between these two sampling methods. However, the silicon analyses of the spoon samples were

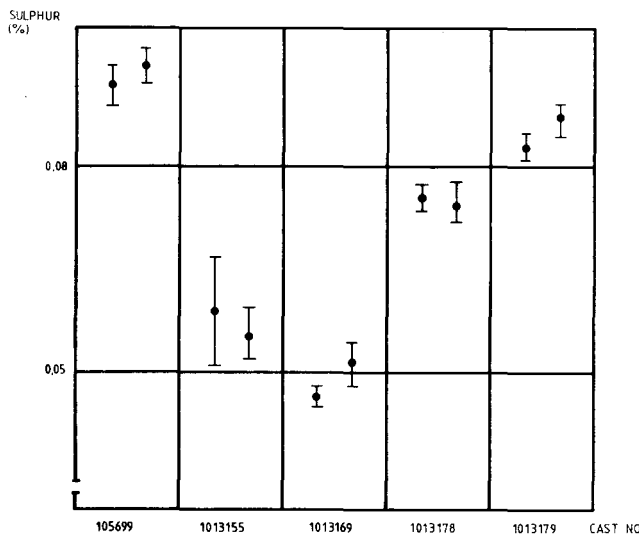


Fig. 2—Average sulphur analyses, with their standard deviations, for spoon and lollipop samples taken from the hot metal after desulphurization. In each column, the lefthand analysis represents the spoon samples, and the righthand analysis the lollipop samples

always lower than those of the lollipop samples. However, as can be seen from Fig. 3, the difference is not significant.

### Steel

The use of spoon sampling for end-point control was established as possible in all situations. Further, it was confirmed that analytically there is no difference between the spoon and lollipop samples as far as their carbon, silicon, manganese, and sulphur concentrations are concerned. The differences were either insignificant or randomly distributed, and the standard deviations were of the same order of magnitude.

However, there were differences in the phosphorus analyses, as shown in Fig. 4, which gives the average phosphorus determinations for samples from four typical low-carbon heats analysed by four different spectrometers. The average analyses of the spoon samples are consistently lower than those of the lollipop samples. Additionally, the standard deviation for the spoon sample is twice that for the lollipop sample. This can be seen clearly from Table I.

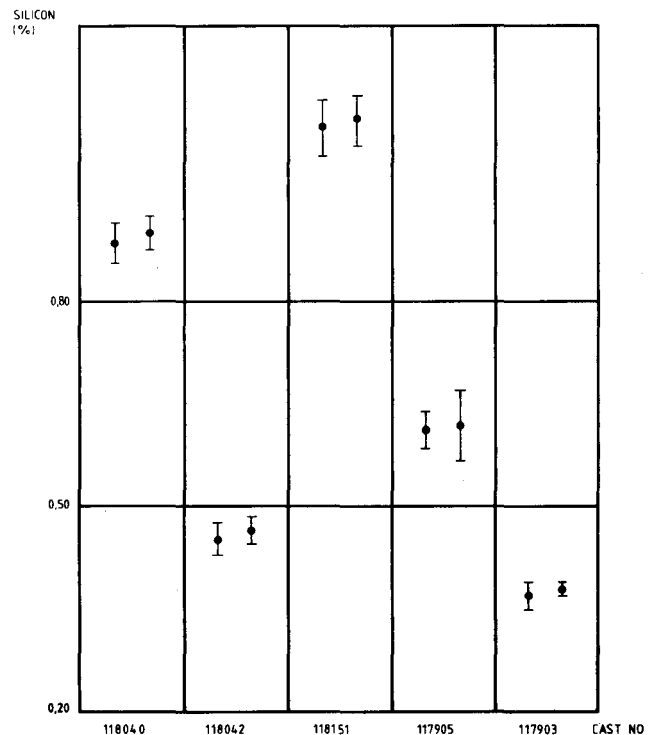


Fig. 3—Average silicon analyses, with their standard deviations, for spoon and lollipop samples taken from the hot metal after deslagging. In each column, the lefthand analysis represent the spoon samples, and the righthand analysis the lollipop samples

TABLE I  
THE STANDARD DEVIATIONS OF THE PHOSPHORUS ANALYSES SHOWN IN FIG. 4

Cast no.	Mean analysis, %		Standard deviation	
	Spoon	Lollipop	Spoon	Lollipop
117347	0,0141	0,0158	0,0018	0,0008
117350	0,0136	0,0150	0,0013	0,0005
117349	0,0058	0,0069	0,0012	0,0008
117354	0,0083	0,0104	0,0011	0,0005

In a comparison of the different deoxidants, it was found that not only an aluminium-killed spoon sample, but also a lollipop with aluminium as deoxidant, gives much lower phosphorus values than a lollipop sample with titanium as deoxidant. There was no difference in the analyses for carbon, manganese, sulphur, and silicon.

With zirconium as deoxidant, there was a definite difference in the sulphur spectrometric analyses between those for titanium- and zirconium-killed samples, the sulphur in the latter always being less than in the former. This is clearly shown in Fig. 5, which gives the results for samples from five typical heats.

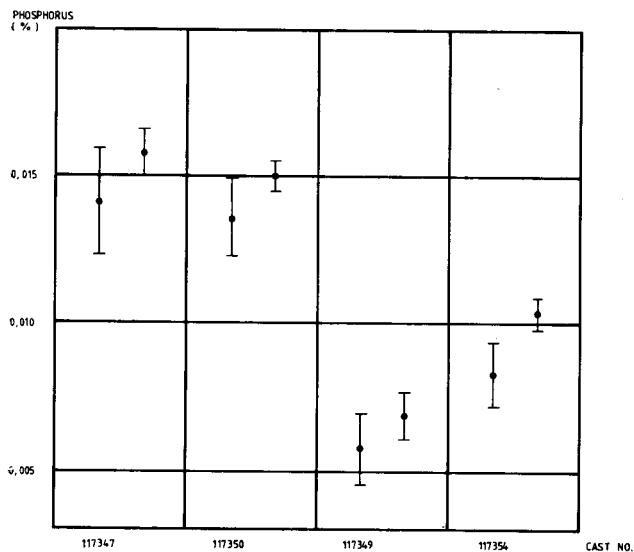


Fig. 4—Average phosphorus analyses, with their standard deviations, for spoon and lollipop samples taken from the B.O.F. at the end point. In each column, the lefthand analysis represents the spoon samples, and the righthand analysis the lollipop samples

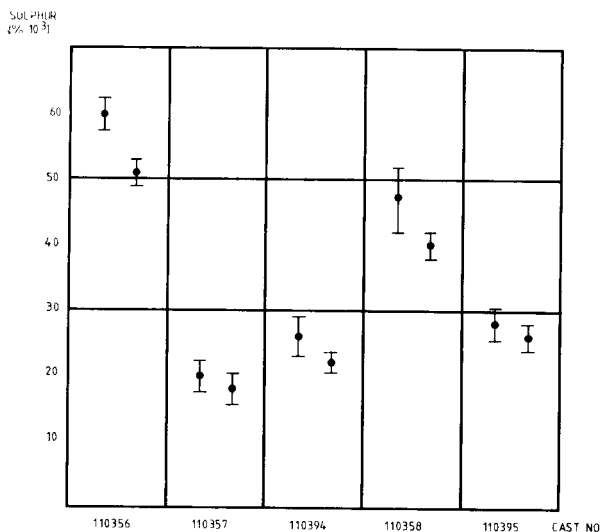


Fig. 5—Average sulphur analyses (made with 4 different spectrometers) of titanium- and zirconium-killed lollipop samples taken from the B.O.F. at the end point. In each column, the lefthand analysis represents the titanium-killed samples, and the righthand analysis the zirconium-killed samples

However, when the same titanium- and zirconium-killed samples were analysed by a Leco carbon/sulphur analyser, there was no difference in the sulphur values. This is demonstrated in Fig. 6, which shows the results of samples from the same heats as those shown in Fig. 5.

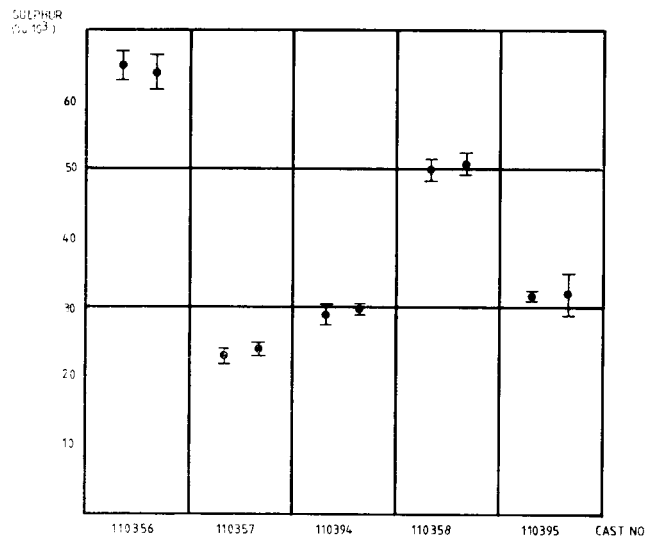


Fig. 6—Average sulphur analyses as in Fig. 5 except that the samples were analysed with a Leco carbon/sulphur analyser

All four lollipop samplers performed reliably, i.e. there was no tendency for the samples taken by any sampler to give consistently different analyses, at least as far as the five main elements were concerned. This was established by a comparison of the mean analyses of the five samples taken by each of the four types of samplers.

The results for samples taken by different samplers varied in consistency. Further, the results for different elements in the samples taken by a certain type of lollipop varied in consistency. However, the difference between good- and bad-quality samplers was clearly apparent in that the good samplers produced samples for which the standard deviation was small throughout.

The success rate of the different samplers when sampling the same heat occasionally varied from 0 to 100 per cent. Generally, the success rate was lower with decreasing carbon content. This exercise clearly showed that there are large differences between various samplers, good-quality samplers giving a high success rate regardless of the carbon level.

### Discussion

As can be deduced from Fig. 1, a reliable sulphur analysis can be obtained from a torpedo whichever of the two sampling methods (spoon or lollipop) is employed. As demonstrated in Fig. 2, this is as true after desulphurization as before, which shows that either no reaction zone remains on the upper part of the hot metal after desulphurization, or that the sample is taken from the same depth with both methods. Further, the standard deviations of the two systems were exactly the same, i.e. either system can be regarded as reliable.

An additional very important factor is the exceptionally high success rate of spoon sampling. When there are

two steel moulds on the copper base plate, two samples can be obtained with one immersion of the spoon. In periods of low hot-metal temperatures, when the success rate of a lollipop sampler is very low, at least one sample is always obtained with the spoon.

As no bias can be expected in sulphur results and as the cost of spoon samples compared with that of lollipops is negligible, particularly if the success rates are considered, a change was made in late 1980 for spoon sampling to be completed at the desulphurization station at Newcastle. Since then, the system has been working smoothly, and no complaints have been received from the operators or from the process laboratory. Additionally, a saving of about R80 000 per year was realized.

It was verified that there is no difference between the spoon and lollipop samples taken at the deslagging station in the analyses for carbon, phosphorus, sulphur, and manganese. However, there is a small difference in the silicon analyses, as can be seen from Fig. 3. This difference is to be expected from the general theory that silicon is the first element that is oxidized from a hot-metal bath. However, such a small constant difference is of no problem, at least to Iscor. The process computer system, in the heat-balance calculations, is designed to correct for any constant deviations in the hot-metal analyses. On the other hand, the temperature of the hot metal at the deslagging station is normally already so low that the taking of lollipop samples has proved to be a very difficult task.

Therefore, as spoon sampling would have to be used in any case when lollipops cease to function at temperatures below about 1250 °C, and as the differences in the analyses are insignificant and standard deviations of the same order of magnitude, it was decided to discontinue the use of lollipop samplers in favour of spoon samplers. No problems have been encountered, and a saving of R40 000 a year was made.

In regard to sampling of steel at the end point, it was verified that spoon sampling is practically possible.

However, there was a big difference in the phosphorus analysis of an aluminium-killed spoon sample and that of a titanium-killed lollipop sample. By the same token, the consistency of the phosphorus analyses of spoon samples was poor, as evidenced by the scatter of the results. All the other analyses of the different elements, as well as the standard deviations, were equal.

Later, a comparison of the deoxidants used in a lollipop sampler showed that aluminium-killed samples give lower phosphorus analyses than titanium-killed samples.

Further, it was established that there is a definite difference in the sulphur analyses between zirconium- and titanium-killed lollipop samples in that the former always give lower values when analysed with a spectrometer. As can be seen from Fig. 5, the difference seems to depend on the sulphur level, i.e. the higher the sulphur level, the greater the difference.

Simultaneously, a much higher failure rate was found in zirconium-killed samplers than in titanium-killed samplers. This is believed to be due to the weaker deoxidation power of zirconium gram per gram since the molecular mass of zirconium is double that of titanium. Hence, double the mass of zirconium is needed to bind

the same amount of oxygen as bound by titanium.

However, when the zirconium- and titanium-killed samples were analysed by Leco carbon/sulphur analyser instead of a spectrometer, no difference could be detected in the sulphur analyses regardless of the sulphur level. With the Leco analyser, the sample is not sparked; material drilled from the sample is burnt in a crucible under oxygen pressure inside a furnace tube.

This cannot mean that the sulphur content of two samples with different deoxidants differs, but rather that the zirconium deoxidant affects the spectrometric analysis. This is probably also true of the phosphorus analysis, i.e. the aluminium deoxidant affects the spectrometric analysis, yielding a lower phosphorus value. The reason for these low measurements is believed to be interference from the peaks of the deoxidant element and its oxides on the intensity of the spark, causing a consistent deviation from the true value. This could be overcome if correction factors were built into the results.

Because of the faulty readings, it was decided that only titanium would be used as a deoxidant. It was thought that this would at least result in products that would not require regrading because of too high a phosphorus or sulphur content.

Secondly, it was decided that the Leco carbon/sulphur analyser would be used as the sole arbiter of sulphur content.

The taking of spoon samples and killing them with titanium wire, instead of the taking of lollipop samples with titanium deoxidant, was considered to be too costly, and the whole idea of spoon sampling for B.O.F. end-point control was abandoned.

The consistencies of samples obtained by different types of lollipops were found to be highly variable. This is surprising when it is remembered that the means of the analyses for the different elements were the same (all the lollipops contained titanium deoxidant). Even when the scatter of the results was wider, the means were the same.

The success rate of different lollipop samplers when sampling the same heat varied greatly. Additionally, for some samplers the success rate was heavily dependent on the carbon content of the bath, in that the lower the carbon content, the lower the success rate.

From this it can be deduced that, in some types of samplers, the amount of deoxidant was sufficient to kill the sample in high-carbon heats when the carbon content was below about 0,05 per cent. Insufficient killing caused the sample to be either full of pinholes or even completely hollow. In the best sampler tested, which had a success rate of 80 per cent down to a carbon content of 0,03 per cent (the lowest carbon content in these investigations), the amount of titanium deoxidant averaged 0,5 g, which is equivalent to approximately 0,006 g of deoxidant per gram of steel in the sample. It is suggested that only this amount of deoxidant can be considered acceptable in sampling for a production of low- and high-carbon steels if a consistently high success rate of lollipop sampling is to be maintained.

Finally, in order to find the most economical sampler, the tender price of each lollipop was divided by its overall success rate. This established that the cheapest sampler was actually the most expensive because of its

low success rate, and the sampler with the second highest tender price was considered to be the cheapest in normal production use owing to its best success rate.

### Conclusions

There is no difference between sulphur analyses obtained on spoon samples and those obtained on lollipop samples from a hot-metal torpedo at the desulphurization station. At the deslagging station, a spoon sample has an insignificantly smaller silicon analysis, all the other analyses being the same.

Spoon sampling can be employed both at the desulphurization station and at the deslagging station.

Spoon sampling from a B.O.F. is practically possible. Aluminium-killed spoon samples have a lower phosphorus analysis than titanium-killed lollipop samples, as do lollipop samples with aluminium as deoxidant as opposed to titanium-killed lollipop samples.

When zirconium is used as deoxidant, the spectrometric analysis for sulphur in a steel sample is lower

than that when titanium is used. Analysis by Leco carbon/sulphur analyser does not reveal any difference between such samples. Thus, it is concluded that the difference in the phosphorus and sulphur analyses are due to the effects of aluminium and zirconium deoxidants respectively on the spectrometric analyses.

Among the different types of lollipops available on the South African market, there are poor- and good-quality products. A sufficient amount of titanium deoxidant in a lollipop sample for end-point control is 0,006 g of deoxidant per gram of sample.

### Acknowledgements

The author thanks the management of Iscor Newcastle Works for permission to publish this paper. Special thanks are due to the production personnel in the steel-plant for carrying out the laborious part of sample taking, as well as to the laboratory personnel at the steel-plant and central laboratories for the analytical service they provided.

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## Corrigendum: February Issue

Figs. 4 and 5 of the paper 'The analysis of ventilation and cooling requirements for mines' by J. van der Walt, E. M. de Kock, and L. K. Smith are positioned incorrectly in the February issue (*J.S. Afr. Inst. Min. Metall.*, vol. 83, no. 2, Feb. 1983). They should have been placed

between pages 32 and 33 (and *not* between pages 36 and 37). The small type in these diagrams is not material to an understanding of the paper, their purpose being to give an idea of the approach adopted in the preparation of ventilation and cooling strategies.

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## Extractive metallurgy of zinc

At a professional development seminar to be held in Montreal (Canada) from 18th to 22nd April, 1983, specialists from industry and university will discuss the extractive metallurgy of zinc from ore to finished metal with special emphasis on the theory and practice of modern technology. Topics will include the mineral processing of zinc ores from conventional and complex sulphides, and the role of image analysis, on-line chemical analysis, and computer simulation in controlling milling practice. Although the pyrometallurgical recovery of zinc from concentrates or residues will be dealt with, the major emphasis will be on electrolytic processes. The Sherrit pressure-leaching process will be compared with conventional roast-leach methods, and the advantages of each discussed. The theory and practice of iron removal, including jarosite, goethite, and hematite processes, will be reviewed, and the critically important subject

of solution purification will be discussed with reference to the control of cobalt, manganese, antimony, lead, chloride, fluorine, etc. Modern tank-house practice and instrumentation will be surveyed in the light of recent plant practice; automated stripping and handling of cathode deposits and the demand that automation makes on cell-room design and operation will also be dealt with. Environmental concerns, such as the control of mercury and arsenic, as well as residue disposal, will be examined. The course will conclude with lectures on the marketing of zinc (and zinc concentrates) and on future prospects for zinc.

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