SAMPLING REFINED COPPER CATHODE USING A SLOTTED PUNCH SYSTEM - A STATISTICAL EVALUATION.

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Abstract

It is known that impurities in copper cathodes segregate to the outer 10mm of the cathode sheet [1]. Consequently, the commonly used sampling method of diagonal punching does not include the correct proportion of edge material. A new automated in-line punching system has been developed at CRL that punches slots from the edge and centre of a cathode sheet in a pattern that provides a sample that is more representative of the whole cathode. This slotted punch system is applicable to both ISA Process Technology and conventional copper cathodes.

Cathode copper taken from different areas of the refinery at CRL has been sampled using this slotted punch system. Chemical analysis of the samples produced has been performed to parts per billion (ppb) levels using glow discharge mass spectrometry (GDMS).

A statistical evaluation of the sources of variation associated with this sampling method (for example, between cathode, between electrorefining cell and between cell sections) has been performed using a mixed Analysis of Variance model based on nested and crossed factors.

The outcome is the development of a new benchmark standard in sampling and analysis, providing customers with the most representative assay for a sample lot and improved confidence in the purchase of electrorefined cathode.

Introduction

The major problem that currently faces both the cathode producer and the consumer is the necessity to confirm specification compliance before universally accepted cathode sampling and analytical methods have been adopted. The overwhelming majority of copper cathode produced is melted and cast into other forms such as cake, billet and continuously cast rod. The most reliable indication of the chemical purity of a cathode lot is the analysis of this melt product. The problem is that the customer requires cathode that complies with a certain specification and the cathode is sold to this specification before any further fabrication.

Since 1997, like many other copper refineries, CRL has not had the large scale melting facilities available at a fabricating operation, making it impossible to analyse the bulk melt product. It has thus been necessary to develop an improved method for sampling manageable quantities of cathode that would provide a representative analysis of a given lot of cathode.

This paper describes a novel slotted punch method of sampling copper cathodes and a statistical evaluation of the sources of variation associated with the method.

Cathode sampling

Cathode sampling involves three basic steps [2]:

1. Random selecting of an adequate number of cathodes that are representative of a lot.

2. Obtaining a sample from these randomly selected cathodes through a mechanical process such as drilling, punching or sawing to a prescribed pattern.

3. Preparing a homogenous portion from the sampled cathodes that is of suitable size and quantity for chemical analysis.

It is known [3,4] that traditional electrolytically refined copper cathode is not homogenous, with the edges of the cathode sheet and loops containing elevated levels of impurities. Work at CRL [5] has shown that for ISA Process cathodes, bismuth is biased towards the top of the cathode, lead, silver, selenium and arsenic are biased towards the bottom of the cathode and sulphur and oxygen are evenly distributed over the body of the cathode but concentrated around the edges. Any cathode sampling technique must therefore reliably capture this variation.

Several cathode sampling techniques have been investigated [6]. These methods typically involve punching, sawing or cutting strips to a prescribed pattern. Punchings offer a simple, flexible method of sampling cathodes, but does not provide a fair representation of the complete cathode because no edge material is sampled. The sawing method includes edge material but leads to a large amount of iron contamination, compromising sale of the sampled cathode. Taking proportional strips (the sampling method recommended by British Standard BS6017 to use in case of a dispute) means that a large proportion of edge material comes form only two cathodes. In addition, the resulting sample, at 40 – 80 kg in weight, is too large to conveniently melt to from an analytical sample in a laboratory furnace.

Since 1986, CRL has utilised a modified sawing method [7] to sample cathode. In brief, 4 vertical and 4 horizontal strips of copper are taken from 8 sheets of cathode. Each strip is then cut into sixths, with the two outer and one inner sixth being retained for analysis. The resulting 24 strips are melted together to form a composite sample for analysis.

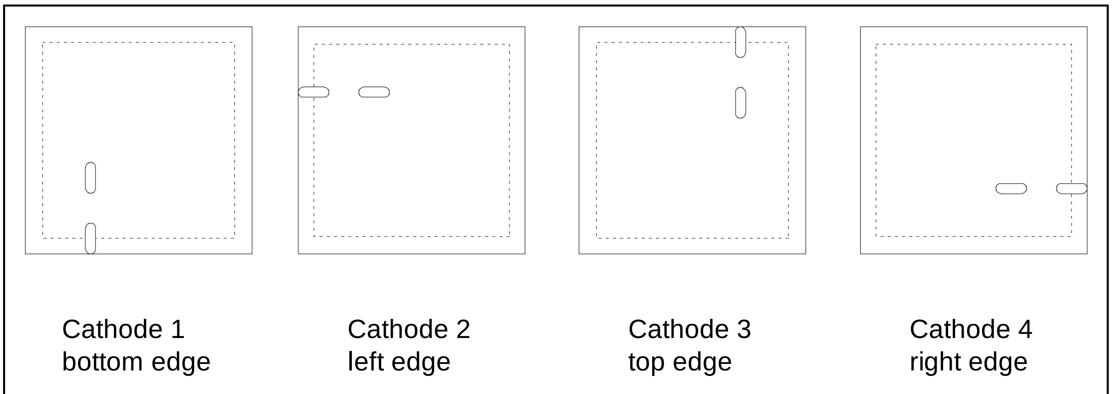
This method is very labour-intensive, involving manual handling of cathode sheets into a shearing machine. In addition, the half sheets left from the shearing process (approximately 1200 kg per week) are scrapped and sent to the anode furnace for recycling. Installation of automatic punching stations on the new cathode stripping machines (CSMs) eliminates both manual handling of cathode sheets and the need to scrap the sampled sheets. An added benefit of the automatic sampling stations on the stripping machines is the greater flexibility associated with the ability to sample at a greater frequency. By taking more samples at predetermined intervals it is thus possible to identify any dependence of variation in analytical data with process conditions.

A statistical evaluation of the sources of variation associated with this sampling method can be performed using a mixed Analysis of Variance model based on nested and crossed factors. The results of this evaluation will then lead to an enhanced sampling regime that can provide a customer with analysis representative of a particular shipment lot whilst providing process feedback to refinery personnel.

Slotted punch pattern

To ensure that those elements that are biased to either the top or bottom of the cathode are effectively captured by the sampling process, slotted punchings are taken from the top, bottom and both edges of the cathode sheet. The punching pattern is illustrated in Figure 1 below.

Figure 1: Illustration of the slotted punching pattern



The die used to punch out the samples from the cathode is 105mm in length and 25mm in width. These dimensions have been calculated to provide a sample with the ratio of edge material to bulk material approximately equal to that found in the cathode. Using the value determined by Mitchell and Whebell [5] (the zone of elevated impurities to be the outer 10mm of the cathode plate), the calculations are below (all dimensions in mm).

Total cathode area = 960 x 960 = 921600 mm^2

Centre area = 940 x 940 = 883600 mm^2

Edge area = 921600 - 883600 = 38000 mm^2

Ratio edge / centre for cathode = 38000 / 883600 = 0.043

Total punch area = 105 x 25 x 2 = 5250 mm^2

Punch edge area = 25 x 10 = 250 mm^2

Ratio edge / centre for sample = 250 / (5250 – 250) = 0.05

It can be seen from these calculations that using the slotted punch method of sampling provides an edge / centre ratio close to that observed in the whole cathode.

Automated sample punching

An automatic sampling station (manufactured by MESCO) is located on each of two cathode stripping machines (CSM) at CRL. The samplers operate in the following manner.

After the stripping operation, cathode sheets are bundled and placed on a walking beam. The top cathode is removed from a bundle of cathodes using vacuum pads and transferred to the punching station. Two samples (one from the edge and one from the centre of the cathode) are punched from the cathode using a K245 tool steel die. The sample punchings fall down a chute and are collected in a box while the punched cathode sheet is returned to the bundle from which it was taken using a second set of vacuum pads. The cycle time for the punching operation is 60 seconds, compared to 4 minutes required to strip enough cathode to form a bundle. This is repeated for four bundles, with each cathode sheet being placed on a turnatable and successively rotated through 90 degrees so that all four edges of the cathode sheet are sampled.

Sample preparation

The cathode punchings forming the samples were melted in a graphite crucible (GE103 grade, Carbon Products of Australia) in an induction furnace (Inductotherm Ltd) to form a composite sample for analysis. The melting took place under a nitrogen atmosphere.

The composite sample so formed was cast into a graphite mould (also GE103 grade) to form a pin sample 8mm in diameter and 20mm in length. This pin was machined using a lathe to remove any surface contamination.

Immediately prior to analysis, the sample was etched in 30% nitric acid, rinsed in distilled deionised water and finally in methanol. Both the acid and methanol were Aristar grade (BDH Ltd).

Sample analysis

The samples were analysed using a VG9000 Glow Discharge Mass Spectrometer (GDMS). This instrument has been described in detail elsewhere [8]. All samples were analysed using a discharge voltage of 1000V and a discharge current of 5mA.

GDMS provides the analyst with full elemental coverage and high sensitivity in the direct analysis of solid samples. Detection limits are typically 0.01ppm or lower. Because of this superior sensitivity, GDMS provides reliable quantitation for elements at levels significantly lower than 1ppm unlike many other trace element analysis methods. This is increasingly important for copper cathode producers, specifically for the analysis of critical elements such as selenium, tellurium and bismuth, where sub-ppm quantitation is required. Table 1 below shows typical detection limits (in ppm) for these elements, compared to the ASTM specification for grade 1 copper cathode.

Table 1: ASTM B-115 Grade 1 Copper Specification Compared to Typical Limits of Detection (in ppm) for OES and GDMS.

Element	Specification ASTM B-115	Typical OES detection limit	Typical GDMS detection limit
Se	2	1	0.01
Te	2	2	0.01
Bi	1	0.5	0.001
Total	3	3.5	0.021

It can be seen from this table that using GDMS provides the cathode producer with increased confidence that the chemical purity of the product meets the required specification.

Comparison between strips and punchings

The first stage of the cathode sampling study was to compare the analysis of samples taken in both strip and punching methods. 30 samples were taken using the automatic punching stations on the new Cathode Stripping Machines (CSMs). Those sheets from which punchings were taken were retained and sampled using the strip method.

Both sets of samples were analysed using glow discharge mass spectrometry, and a paired t-test performed on the results. A paired t-test examines the difference between pairs of results given by two methods. It is used in this study for two reasons: the test samples are essentially from different sources (tankhouse sections) and have varying concentrations; a paired test removes the effect of variation in environmental conditions [9].

The results are summarised below in Table 2. The average of the 30 analyses obtained using both strip and punching methods, along with the t value, is shown for each element.

Table 2: t-Test Comparison between cathode samples produced by CRL modified Strip method and Slotted Punch Methods.

Element	**Strip**	**Punch**	**t**
Ag	11.0	10.9	0.72
As	0.43	0.46	-0.94
Bi	0.10	0.08	1.58
Cd	0.02	0.02	1.53
Co	0.02	0.02	0
Cr	0.02	0.03	-1.63
Mn	0.01	0.01	0
Ni	0.45	0.48	-0.55
P	0.03	0.02	2.1
Pb	0.07	0.07	-0.24
S	4.3	4.4	-0.1
Sb	0.16	0.16	0.69
Se	0.05	0.06	-1.38
Si	0.05	0.10	-1.38
Sn	0.02	0.02	-0.37
Te	0.07	0.06	0.52
Zn	0.04	0.06	-2.45

At 95% confidence, a t value less than +/- 2.04 indicates that there is no statistical difference between the two sets of data and the two methods give the same result [9]. At 99% the t value rises to +/- 2.75.

It can be seen from the above table that the only elements that have statistically different results at the 95% confidence level are phosphorus and zinc, but these elements are present at such low levels in CRL cathode that the difference is of no consequence. At the 99% confidence level both sampling methods give the same average result for all elements. The data in this table also highlights the performance of GDMS at levels significantly below 1ppm.

The existing strip method of cathode sampling at CRL has been shown to provide a good representation of the melt sample. It follows that the slotted punch method described in this paper will also provide a representative sample of a cathode lot.

Section sampling

An added benefit of the automatic sampling stations on the stripping machines is the greater flexibility associated with the ability to sample at a greater frequency. By taking more samples at predetermined intervals it is thus possible to identify any dependence of variation in analytical data with process conditions.

The tankhouse at CRL consists of 1162 electrorefining cells, arranged in 37 sections. These sections in turn are divided between 3 discrete electrolytic circuits. Using the ISA process at CRL, copper is deposited onto stainless steel cathodes. The life of a copper anode is 21 days, with most copper cathodes being harvested in three crops every 7 days. Approximately 10% of copper cathodes are harvested in two crops of 10 and 11 days.

Sample punchings were taken from every section of the tankhouse for a period of three months. These samples were analysed using glow discharge mass spectrometry. In all, a total of 326 samples were included in this study. The average and standard deviation of all test results are shown in table 3.

Iron and silicon are not shown as they are subject to contamination from the sample punch and melting in the crucible. The only elements that showed significant variation with the factors studied here are silver, arsenic, bismuth, nickel, lead, sulphur and antimony. Only these elements have been included in the statistical calculations that follow.

Table 3: Average and Standard Deviation for all GDMS Test Results.

Element	Average (ppm)	SD (ppm)
Ag	11.2	2.6
As	0.69	0.47
Bi	0.12	0.10
Cd	<0.1	
Co	<0.1	
Cr	<0.1	
Mn	<0.1	
Ni	0.63	0.46
P	<0.1	
Pb	0.15	0.14
S	6.3	2.6
Sb	0.20	0.12
Se	0.06	0.04
Sn	<0.1	
Te	<0.1	
Zn	<0.1	

Analysis of variance

In the case of section sampling, the samples come from different areas of the tankhouse, introducing a controlled error. Other controlled errors include electrolytic circuit, cathode crop and cathode age (7/10 day). In this case, a simple t-test is insufficient to provide statistical information on the samples. A more powerful technique needs to be used to determine whether the observed variation is due to random or controlled factors. Analysis of variance (ANOVA) was used to separate and estimate the different causes of variation in the results. ANOVA is used in this study to separate any variation caused by changing the controlled factor from the variation due to random error. It can thus test whether altering the controlled factor leads to a significant difference between the mean values observed [9].

ANOVA calculations involve mean squares – a sum of squared terms divided by a number of degrees of freedom. The total variation can be calculated by summing the squares of the deviation of each result from the overall average result and dividing by the total number of degrees of freedom. The variation between group can be calculated by summing the squares of the deviation of the mean result for each group from the overall average result and dividing by the number of degrees of freedom between groups. The variation within each group can be calculated by summing the squares of the deviation of each result within a group from the average group result and dividing by the number of degrees of freedom within a group. The between sample mean square is then divided by the within sample mean square to give an F value. If this F value is greater than a critical value F_{crit} then the variation between groups is significantly greater than the variation within a group.

ANOVA has been used to separate and estimate the sources of variation associated with the tankhouse parameters mentioned above. Each parameter is dealt with in turn. Tables 4 to 7 list the F values returned from ANOVA calculations for each element and compares them with a critical value. All ANOVA calculations were performed at the 99% confidence level.

Variation between circuits

Three discrete electrolytic circuits are used at CRL. These circuits have separate volumes of electrolyte and are electrically isolated form one another.

Table 4: ANOVA Analysis of the Variation Between Circuits

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
0.71	2.05	0.69	1.42	0.63	1.29	2.17	3.02

The F values for all elements are less than $F_{crit.}$ This indicates that there is no significant variation in cathode purity between circuits. The main sources of variation between circuits would be differences in refining power and differences in the chemical composition of the three electrolyte streams. During this study, all three circuits were operating at a constant refining power. The chemical composition of the electrolyte from the three circuits was similar, the difference in composition being less than 5% across the circuits.

Variation between sections

The three circuits at CRL are divided into 37 separate sections. These sections can be independently switched in and out of the electrical circuit during electrode loading and unloading.

Table 5: ANOVA Analysis of the Variation Between Sections

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
0.40	0.76	1.24	0.79	1.16	0.79	1.00	1.49

The F values for all elements are less than $F_{crit.}$ This indicates that there is no significant variation in cathode purity between sections. This result is not surprising because the source of variation between sections is the same as for between circuits.

Variation with crop

As mentioned above, 90% cathodes are harvested from a single anode in three crops of seven days cathode growth. For the calculations reported here, only seven day crops have been considered.

Table 6: ANOVA Analysis of the Variation Between Cathode Crop

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
147.1	1.30	3.11	1.17	3.64	1.28	0.58	2.40

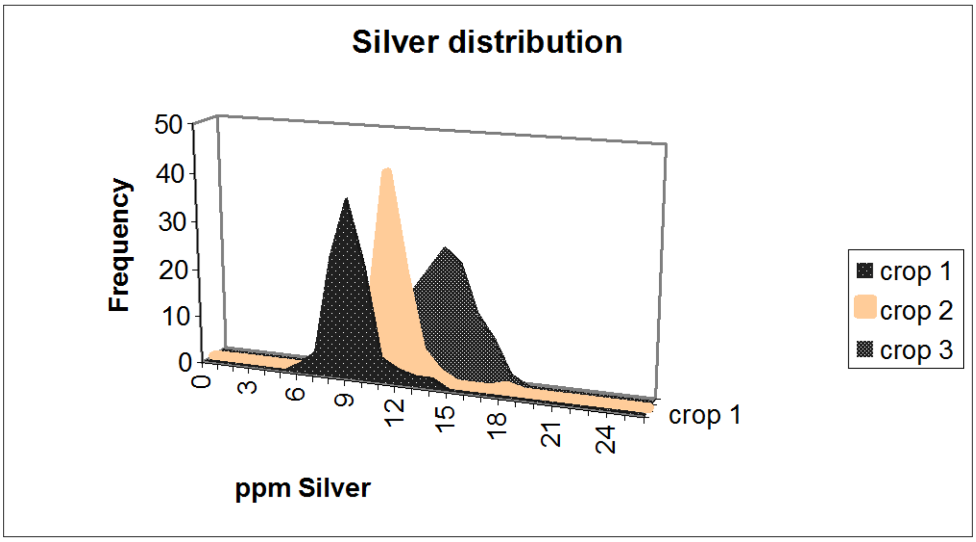
The F values for silver, bismuth and lead are greater than $F_{crit.}$ This indicates that for these elements there is a greater variation in cathode purity between crops than within a given crop.

The magnitude of the F value provides an estimate of the magnitude of the variation. The dependence of silver on crop is by a long way the strongest seen in this study. This is highlighted in Figure 2 below which shows the distribution of silver.

This clearly shows that each crop has a distinct range of silver concentrations, with crop1 cathode having the least silver (average 8.9ppm), increasing for crop 2 (average 10.8ppm) and crop 3 cathode the highest (average 13.7ppm). It is generally considered that this is a result of the increased electrode spacing encountered from crop1 to crop2 to crop 3. The increased cell voltages form crop 1 to crop 3 creates increasing electrolyte temperatures from crop 1 to crop 3 which leads to a corresponding increase in the silver contenst of the cathode produced.

There is also a small statistical difference in the lead content of the cathode from different crops. Lead follows the opposite course with crop1 the highest (average0.18ppm), dropping for crop 2 (average 0.15ppm) and crop 3 the smallest (average 0.12ppm).

Figure 2: Observed Variation in Silver Distribution Between Cathode Crops



Variation with cathode age (7 / 10 day cathode)

As mentioned previously, most copper cathodes are harvested in three crops, of 7 days. Approximately 10% of copper cathodes are harvested in two crops of 10 and 11 days. The difference between the two cathode ages has been examined.

Table 7: ANOVA Analysis of the Variation Between Cathode Age

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
0.70	1.80	7.54	1.59	2.48	0.01	1.56	3.87

The F value for bismuth is greater than $F_{crit.}$ This indicates that the variation in cathode purity between 7 and 10 day cathode is greater than that within each age. The average level of bismuth in 7 day old cathode is 0.11ppm, while in 10 day old cathode the bismuth concentration is, on average, 0.17ppm. The mechanism for this is unclear at present, but a similar effect has been seen at other refineries.

Weekly variation

While any variations that may be seen from week to week may not strictly be a controlled factor, ANOVA calculations can still be performed to investigate whether there is a significant variation in cathode purity with time.

Table 8: ANOVA analysis of the Weekly Variation

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
1.11	3.20	1.00	3.26	4.22	6.52	2.21	1.75

The data shows that during the 14 weeks of this study, there was significant variation in cathode purity from week to week for most elements – only silver and bismuth do not show significant variation. This can partly be explained by the fact that arsenic, nickel and sulphur do not show any variation with other controlled factors under study here. With the exception of copper, these three elements are the most abundant in CRL electrolyte. It can be concluded that the distribution of these elements is affected by other random variables that lead to entrapment of electrolyte into the cathode growth.

Lead also shows significant variation with time. As lead is insoluble in electrolyte, the only mechanism by which it can report to cathode is by the entrapment of anode slimes. Likewise, the observed variation must be due to random effects that lead to slimes entrapment in cathode.

Within section sampling

A total of 88 samples were taken from every bundle of cathode produced from one section of the tankhouse over three separate crops. An F-test was applied to the data produced from the analysis of these samples. The average variance across all three crops was taken to negate the effect of differences between crops. The variance of the results obtained for samples taken from within the section was compared with the variance from all sections. The F values are listed in Table 8 below. Where the F value for an element exceeds the value of F_{crit} then the variance within the section is significantly less than the variance for all sections.

Table 8: F-Test Analysis for Within Section Sampling

Ag	As	Bi	Ni	Pb	S	Sb	F_{crit}
2.17	20.3	6.20	23.5	3.33	3.15	6.89	1.72

The data shows that the variation from one section to the next is greater than the variation between cells in the same section. The main source of variation within the tankhouse is between sections, rather than within any individual section. The effect of factors such as differences in electrolyte flow between cells of the same section is less than the effects due to factors described previously. Consequently, the extra effort required to sample at a frequency greater than one per section is not necessary.

Comparison between actual and reported results

The current sampling regime is to take one sample per week per circuit. These samples are analysed using GDMS and the assay results entered into the laboratory database. This is a hangover from the days when 40% of the cathode produced at CRL was cast into rod on site and extensive sampling of the rod occurred. Since rod production ceased, this has left a deficiency in the cathode sampling.

Table 9: Comparison Between Section Sampling and Previous Assay Reporting System

	SWC	Ag	As	Bi	Ni	Pb	S	Sb
	LDB	**13.2 +/- 1.6**	**0.9 +/- 0.6**	**<0.1 +/- <0.1**	**0.8 +/- 0.4**	**<0.1 +/- <0.1**	**5.6 +/- 2.4**	**0.2 +/- 0.1**
1000t (4)	A	11.2 +/- 1.6	0.89 +/- 0.28	0.06 +/- 0.02	1.0 +/- 0.5	0.08 +/- 0.03	7.8 +/- 2.9	0.16 +/- 0.01
500t (3)	B	11.4 +/- 2.2	1.3 +/- 1.0	0.04 +/- 0.02	0.86 +/- 0.41	0.15 +/- 0.11	11.7 +/- 7.2	0.17 +/- 0.07
100t (1)	C	11.8	1.9	0.19	1.6	0.42	2.5	0.21
100t (1)	D	13.7	0.21	0.03	0.30	0.06	2.7	0.30
100t (1)	E	7.8	0.36	0.03	0.29	0.09	3.9	0.14
100t (1)	F	8.5	0.49	0.04	0.38	0.18	5.3	0.14
250t (2)	G	11.4 +/- 2.9	1.0 +/- 0.51	0.10 +/- 0.08	1.3 +/- 0.3	0.11 +/- 0.04	5.6 +/- 1.8	0.17 +/- 0.08
250t (2)	H	13.6 +/- 3.0	0.74 +/- 0.04	0.05 +/- 0.01	1.3 +/- 0.7	0.13 +/- 0.02	5.3 +/- 0.2	0.21 +/- 0.01
500t (2)	I	9.6 +/- 3.1	0.53 +/- 0.11	0.07 +/- 0.05	0.88 +/- 0.45	0.06 +/- 0.01	4.9 +/- 2.7	0.15 +/- 0.01
200t (1)	J	12.3	0.57	0.04	0.60	0.17	7.9	0.18
300t (1)	K	9.8	0.76	0.19	0.44	0.32	9.6	0.43
300t (3)	L	12.3 +/- 2.5	0.66 +/- 0.23	0.43 +/- 0.47	0.45 +/- 0.18	0.14 +/- 0.07	6.4 +/- 1.2	0.53 +/- 0.58

At present, the method of reporting results is as follows:

A Sworn Weigher's Certificate (SWC) for a shipment is prepared according to customer requirements. This SWC will consist of a number of bundles, taken from one or more sections in the refinery, depending on the size of the lot. The date of the SWC is entered into the database. This automatically generates an assay certificate for the shipment that is the average of the previous four weeks production.

For all of the samples taken in this study, the corresponding SWC was noted. A comparison between the average LDB assay and the individual SWC assay has been performed for a shipment of cathode. Because all SWCs relate to the one shipment on the same date, the LDB assay is the same for all lots.

Table 9 shows that the assays based on SWC numbers are, in certain cases, statistically different to the average data shown on the assay certificate produced by the laboratory database. In other words, the assay certificate is not always a true representation of the chemical composition of the cathode received by the customer. Taking samples on a section basis will provide the customer with a more representative assay of the shipment lot.

Conclusions

A method of sampling copper cathodes using a slotted punch has been described. This method takes account of material from the cathode edges, thus providing a sample that is representative of a complete cathode plate. This sampling method provides a sample that is statistically the same as the previous method used at CRL, which has previously been shown to provide a sample representative of a lot.

A statistical evaluation of the samples taken over a three month period has shown that the silver content of cathode is dependent on the cathode crop and that bismuth content is dependent upon the age of the cathode growth. Other elements such as arsenic, nickel, sulphur and lead show a dependence upon “random” factors relating to entrapment of electrolyte or anode slimes in the cathode. The variance of sampling cathodes within a section was found to be less significant than the variance from section to section. The optimum sampling frequency at CRL is to take a sample for every section.

Combined with the unrivalled sensitivity of GDMS, this method provides a powerful and flexible sampling and analysis regime that provides process feedback to refinery personnel and gives the customer increased confidence that cathode production meets LME specifications.

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