Current distribution in modern copper refining

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ABSTRACT

In today's modern copper electro-refineries, increasingly higher average current densities are being employed. With these increases many refineries are approaching their limiting current density. The nearness of the average operating current density to the limiting current density has placed increasing emphasis on the need to maintain an even current distribution. This paper explores the importance of maintaining even current density and discusses the factors, processes and practices that are necessary to achieve and maintain high quality production at high operational intensity.

INTRODUCTION

The copper industry was based essentially on the use of a copper starter sheet as the substrate for the refined copper deposition. In the 1970's operating current densities with this technology were typically around 220-250 amps per square metre.

There was a clear recognition that the maintenance of electrode spacing or geometry was crucial in minimising short circuits and rough growth within the cells. A number of systems aimed at rigidising the fragile copper starter sheets were introduced. These included a number of both pre and post-installation straightening systems including starter sheet embossing and restraightening systems such as the PD press.

The pursuit of the vertical electrode culminated in the introduction of permanent stainless steel technology by the ISA PROCESS^{TM} group in 1979 at MIM's Townsville Refinery. The introduction of this inherently straight permanent cathode technology led to its combined use with high quality anode straightening machinery and crane placement systems. These combined systems led to very predictable electrode geometry and inter-electrode gaps, resulting in superior cathode quality at high current density.

The industry now had a refining system, which had overcome much of the labour intensive tasks associated with maintaining correct and even electrode spacing.

Limiting Current Density

A key industry target has been to increase productivity and reduce costs while improving product quality. Increasing current density has been an important element of this aim, along with larger electrodes, closer spacing, larger numbers of plates per cell and higher time efficiency.

The maximum current density possible is related to the ability of cupric ions to migrate to the cathode surface as quickly as those ions can discharge from the anode. This is driven by the diffusion rate of cupric ions across the boundary layer at the cathode face. The thickness of the boundary layer depends on many factors including flow rate of the bulk electrolyte and the concentration gradient across the boundary layer. This process is described by Fick's Law (1), which can be written as;

$$\frac{-dQ}{dT} = \frac{D(C_b - C_e)}{d} \tag{1}$$

where C_b is the concentration of the cation (cupric) in the bulk solution (mol/m^3), C_e is the concentration of the cation at the electrode surface, d is the distance over which the concentration change occurs (m), D is the diffusion coefficient (m^2/s). dQ/dT is the flux in $mol/m^2/sec$.

If the current density exceeds the ability of cupric ions to diffuse across the boundary layer the current will be carried by cations other than copper, and a reaction other than copper reduction at the cathode will occur. The limiting current density can be written as the equation;

$$i_{lim} = \frac{nFDC_b}{d} \tag{2}$$

where i is the current density (A/m^2), F is Faraday constant (C/mol) and n the number of moles of electrons in the electrochemical reaction.

This condition exists when the cupric ion concentration is zero at the electrode. If more current is driven through the electrode it will be carried by cations other than copper. In electrorefining, this would normally be Arsenic and possibly Bismuth or Antimony.

A key factor here is that the limiting current can be reached at any electrode, or part of an electrode in a cell, prior to the full set of electrodes reaching their limiting current. This results in the generation of a rough and open structure in the high current density regions. This cathode will not comply with the criteria specified by international standards. Rough growth in turn can result in the inclusion of slimes and electrolyte within the structure. Both occurrences will result in non-compliant product.

Quality Considerations

In a copper market where demand outstrips supply, the minimum standard is often sufficient. However in a less favourable market, only suppliers of the highest quality copper will maintain full sales of their product and achieve maximum premiums over standard product value. In the modern era, downstream fabricators are under constant pressure to reduce their costs. These companies are becoming less inclined to accept the need for rework due to poor raw material supply.

Table I – Cathode Quality Standards versus Typical ISA PROCESS^{TM}

Element	LME Limit ppm	ASTM B115 (COMEX) Limit ppm	Xstrata Refinery (12 month average) ppm
Pb	5	8	0.1
As	5	5	0.5
Sb	4	5	0.2
Bi	2	2	<0.1
Ag	25	25	12
S	15	25	5
Fe	10	12	<0.1
Ni(+other)	20	8	0.6
Se	2	4	<0.1
Te	2	2	<0.1

While the LME and Comex standards are recognised internationally as good supply, copper producers are now aware that simple compliance is not enough. Some of the world's key wire-rod producers will simply not accept sulphurs above 5 ppm. Lead concentrations should be maintained well below 3 ppm.

Current Distribution - Theory

Electrode pairs in a cell are arranged in parallel with the direction of current flow, such that total cell current divides between the electrode pairs in accordance with Ohms Law. The current passing through each electrode pair is inversely proportional to its component resistance.

Ideally, if all resistance paths are equal, the cell current will divide so that all the electrodes will operate at the mean current density over the entire surface of the cathode. In practice however, variations in ohmic resistance between electrode pairs leads to non-uniform current distribution. The range of current densities within each cell approximates a 'normal' distribution. Cathode plates at the extreme high end of the range are the first to exhibit rough growth and ultimately cause short circuits. These highs also restrict the ability to raise the mean current density because they impact on the current efficiency and cathode quality.
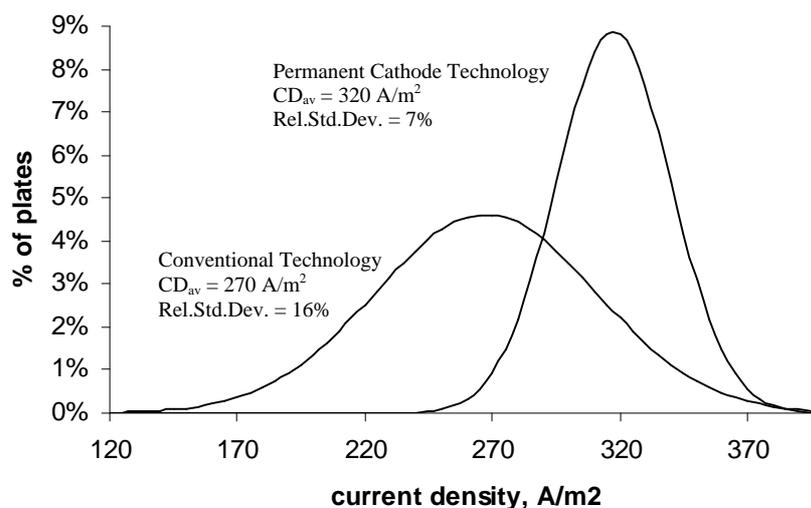
Figure 1 – Current Distribution Comparison - Conventional and Permanent Cathode

Factors affecting Current Distribution

The causes of non-uniform current distribution are simply those physical characteristics that affect the electrode pair resistance, namely;
- Electrode cell spacing
- Electrode alignment
- Electrode physical geometry
- Electrode contact resistance
- Electrode internal resistance

The factors that have greatest impact on current distribution will be those which contribute the greatest component voltage to the overall cell voltage.

Table II – Cell voltage Components, typical modern refinery*

	Components of Cell Voltage, mV		
	Crop 1	Crop 2	Crop 3
Anode contact voltage drop	10	10	15
Electrolyte voltage drop	220	270	320
Cathode plate internal resistance	25	25	25
Cathode plate contact	25	25	25
Anode overpotential	-340	-340	-340
Cathode overpotential	340	340	340
Total Cell Voltage	280	330	385

* permanent cathodes, 600 Amps/plate (300 A/m^2) electrode pitch 100mm

Electrolyte Resistance

Electrolyte resistance is by far the major component, representing 80-85% of total cell voltage. Therefore small changes electrode geometry that affect inter-electrode gap will have a major impact on the electrode pair resistance and current distribution. Electrode spacing and geometry are the key variables that must be controlled to optimise current distribution. This is particularly true in modern high-intensity refineries that use increasingly thicker anodes and closer electrode pitch. As anode thickness increases, the current distribution becomes increasingly sensitive to variations in inter-electrode gap.

Electrode Contact Resistance

In a modern refinery, the average cathode plate contact voltage accounts for 8-10% of the overall cell voltage. However contact voltage is often highly erratic, depending on the physical condition of the contact surfaces. Field measurements show that individual contact resistance typically ranges from 20-200 µO, equivalent to 5%-25% of total cell voltage. Cell contacts can therefore have a substantial effect on current distribution if not correctly managed.
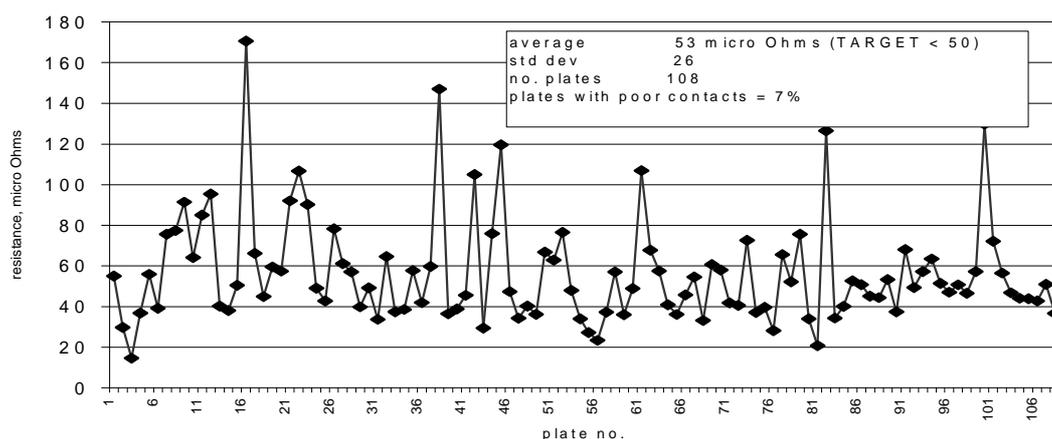

Figure 2 – Cathode Plate Contact Resistance

Electrode Internal Resistance

Cathode plate internal resistance depends upon the plate design characteristics. A typical ISA PROCESS[TM] plate accounts for around 8% of total cell voltage. However more important is the ability of the cathode plate to maintain low resistance over the duration of its life. Inferior plate designs result in a marked deterioration of electrical properties over time. Therefore plate internal resistance becomes a significant component in the overall cell voltage, and variable plate resistance will impact current distribution.

Anode resistance (both internal and contact resistance) is typically less than 2% of the cell voltage and therefore has negligible effect on current distribution.

OPTIMISATION OF CURRENT DISTRIBUTION

Electrode Alignment

Electrode geometry and alignment have long been recognised as the essential requirements for producing high quality cathode at high current density. With the use of increasingly narrow inter-electrode gaps, small deviations in electrode spacing have a proportionately larger impact on the inter-electrode gap and therefore on current distribution.

The aim of alignment is simple in theory. Anodes are placed at a fixed and uniform pitch in the cells, using the mould face of the anode lugs as a reference. Plates are then interleaved so that the blade is equal-distant from each adjacent anode face.

Alignment practice is carried out either automatically with advanced crane systems, or manually by the tankhouse operators. Both methods are capable of good results when implemented correctly. The main benefit of crane alignment is consistency and repeatability.

Manual alignment techniques commonly employed include the following;

Torching in – The gap between anode and cathode blades is checked visually with the aid of a hand-held light during the anode change, without electrolyte in the cell. This time-consuming method is most useful when anode physical quality is poor.
Visual Spacing – Anodes and cathodes are positioned in relation to reference points on the cell-top furniture (insulators and / or contact bars).
Spacer tools – A hand-held spacer bar is used to re-position the cathode hanger bars to a set distance from the mould face of the anode lugs (equal to the theoretical spacing for nominal anode thickness).

Some modern operations have the capability of automatically aligning the electrodes, such that little or no manual adjustment is necessary. This requires integration of the anode preparation machine, cathode stripping machine and overhead cranes, such that;

➢ The anode preparation machine and cathode stripping machine deliver electrodes to the crane at precisely the correct pitch. Anodes are positioned via the 'mould' side, which has less physical variance than the 'set' side.
➢ The crane is capable of maintaining the electrode pitch during loading / unloading and during transit. The crane hooks must positively locate the cathode plate hanger bars and have minimal free tolerance. Hooks must be robust enough to resist bending.
➢ Final placement (fine-positioning) of the crane bale on the cells must be highly accurate. Positioning devices used include laser targets and the more positive mechanical systems (cone or pyramid). 'Stiff-leg' cranes facilitate location of the bale onto the positioning device.

- The position of the cathode hooks relative to the anode hooks must be adjusted to the correct spacing, and checked by actual observation of the cathode. This action must be precise and repeatable.
- To enable the crane system to function as designed, the cells and cell-top furniture must be positioned accurately and remain fixed in place.

Xstrata's refinery in Townsville has operated two fully automatic cranes since it underwent a major refurbishment in 1998. These cranes are highly reliable and consistently place the electrodes within 2mm of their intended target. The alignment capability of the anode preparation / cathode stripping machine / overhead crane system is checked daily, by placing one set of electrodes in a calibrated portable rack.

Anode Quality

Variable anode geometry has a significant impact on inter-electrode gap and therefore current distribution. To fully realise the benefits of permanent cathode technology, significant improvements to anode quality were needed. Anode geometry had become a limiting factor in refining performance, which led to improved casting practice and better anode preparation.

There is now greater onus on casting operators to deliver anodes of consistent weight that are free from bowing, taper, fins or wash. A five percent variation in anode weight can result in blade thickness variation of 2-3mm. This is significant in high intensity refineries where inter-electrode gap may be less than 20mm on crop 1[1]. Modern weight-controlled casting systems are capable of delivering weight control within 2% of the target.

Key improvements to the anode preparation machines include lug contact milling, face milling and lug centring. More sophisticated machines also measure lug and blade thickness at various points in the press, and reject / accept anodes based on thickness, taper and other dimensional criteria.

Lug face milling and lug centring reduces interference between lugs that would otherwise prevent proper alignment, particularly in high-intensity cells with narrow gaps. These features also facilitate crane handling by ensuring the anode lugs are compatible with the crane hooks. Lug centring also aids manual alignment by allowing operators to more easily judge by eye the correct position of the lug. This can be difficult with off-set lugs.

A further contribution to improved alignment comes from the introduction of narrower cathode plate hanger bars, made possible by the high strength of the stainless steel hanger bars system. ISA PROCESS[TM] has supplied hanger bars to a width of 25mm in response to customer requirements. The strength of the stainless steel hanger bar

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[1] Based on ISA PROCESS plant operating with 400kg anode and 95mm pitch

ensures the mechanical properties and geometry of the plates will not be compromised over time.

Operating Cycles

Permanent cathode technology offers greater flexibility with stripping schedules than can be achieved with conventional technology. Anode / cathode cycles can be varied to suit operational requirements. A practice commonly used in high intensity refining is to vary the anode / cathode cycle to optimise current distribution, including;

➢ Reducing the anode weight and cycle time, to increase average inter-electrode gap. Anode cycles from 14 to 21 days are used amongst ISA PROCESS™ operators. Example – 5d / 5d / 6d (crop 1 / crop 2 / crop 3)
➢ Shortening crop 1 duration and extending crop 3 duration, to maximise current efficiency (inter-electrode gap increases with crop number). Example – 6d / 7d / 8d
➢ Shortening crop 3 duration, to minimise poor current distribution arising from light anode scrap / poor anode contacts in latter crop 3. Example – 6d / 8d / 7d
➢ Converting to a 2 crop operation instead of the traditional 3 crop operation. This reduces anode weight and therefore inter-electrode gap. Example 7d / 7d. (Often two crops are used to achieve other objectives such as increased cathode weight, or reduced workload on the machines – Example 10d / 10d).

Electrode Geometry

The single most significant property of permanent cathode technology is the vastly improved plate geometry. This is particularly well demonstrated by the benchmark ISA PROCESS™ refineries around the world.

Performance of traditional refineries was constrained by the poor cathode geometry inherent with copper starter sheets. This was despite innovations such as embossing, rigidising and pressing of the starter sheets. Permanent cathode technology provided the step-change improvement in cathode geometry that was needed to make high intensity refining possible.

Cathode Plate Verticality

Verticality of the cathode plate is essential for achieving uniform current density over the face of the cathode plate. Non-vertical plates are subject to localised high current density in the bottom portion of the plate, leading to rough growth, increased entrapment of impurities, proximity shorting, and lowering of the effective limiting current density.

In modern refining with narrow inter-electrode gaps, small deviations in verticality can have significant impact on current distribution. A plate that is hanging 6mm off-plumb will raise the current density by a factor of 30% in the lower region of

the plate[2]. As the intensity of refining increases, demands on plate verticality become greater.

Manufacturers of quality cathode plates should achieve verticality tolerance at least ± 5.5mm (centre-line deviation from vertical). Operators are demanding even stricter verticality tolerance in some operations.

While construction tolerances are important, the ability of the plate to maintain its geometry in service has a far greater impact on long-term plant performance. Plates must be robust enough to resist bending. The hanger bar system is a critical design feature that imparts overall strength to the plate, and provides rigidity to the blade. Hanger bar systems can be either copper or stainless steel. A copper-plated RHS stainless steel hanger bar, welded to a high chemical and physical quality stainless blade, has proven to produce the most consistent long-term performance.

Proper management of process parameters including electrolyte composition and reagent levels, will preserve the blade surface condition and maintain copper stripability. This in turn minimises mechanical damage during stripping.

Routine checking of plate verticality is also highly important. Non-vertical plates can generally be repaired on site using a simple peening technique.

Anode Verticality

Anode verticality is equally important as cathode verticality. Traditionally anode verticality was often achieved by inserting packing under the lugs to alter the hang of the anode, during torching-in.

Significant improvements were made with the introduction of pressing and contact milling in the anode preparation machines, as highlighted already. Lug pressing should incorporate re-setting of the lugs to the centre of the blade. Measurements have shown (2) that anodes with off-set lugs tend to hang 7-8mm off-plumb, and this can be overcome by centralising the lugs.

Contact milling improves verticality by providing a flat, regular contact surface. Correct maintenance and set up of the milling equipment and cutting heads is critical.

Cathode Plate Flatness

The inherent flatness of stainless steel cathode blades is a key factor in the success of permanent cathode technology. Today's manufacturers can supply to a flatness tolerance of 3mm. However, the on-going flatness of the plate is more important

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[2] assuming 17mm inter-electrode gap, crop 1

than the original flatness tolerance. This is a function of blade thickness, hanger bar type and plant operating conditions.

A blade thickness of 3.25mm for most applications has proven to be the most cost-effective, in terms of current efficiency, plate maintenance costs and ultimate service life.

The hanger bar system provides much of the overall strength and rigidity to the overall plate assembly. Alternative hanger bar systems provide varying degrees of strength, however it is generally held true that stainless steel hanger bars provide optimum strength and durability. While solid copper hanger bars are widely used, a long-term bond between the copper bar and the stainless steel blade continues to elude manufacturers.

Plates that are bent or bowed may be tolerated provided they hang within an acceptance envelope (eg 14mm for a 3.25mm plate). The allowable envelope becomes tighter as current density increases or electrode pitch decreases. The decision to straighten a bowed plate should be based on hang-test results rather than absolute blade flatness.

On-going management of cathode plates is the key to their long term performance and extended life. Mechanical damage to the cathode plates can occur during crane handling, in the stripping machines, or through manual handling during repair and manual stripping. Areas that are often problematic include;

➢ Plates can collide with anodes or cell walls during cell loading, or strike feed conveyors during machine loading. Cranes should have accurate bale positioning, and incorporate sensors, which stop the bale from lowering when 'plate-high' is detected.
➢ Stripping machines must be engineered and set up to eliminate impact points. Automatic hammering of cathode plates to remove difficult-to-strip copper is not recommended by the ISA PROCESS^{TM} as it can stretch and deform the plates.
➢ Incorrect manual stripping techniques have the potential to cause severe mechanical damage to the plate, which can affect its hanging geometry.

Cathode Plate Contact Resistance

Contact Maintenance

The contact resistance of individual cathode plates typically accounts for between 5% and 25% of the overall electrode pair resistance. The large variation is due to the high sensitivity of plate resistance to the condition of the contact surface.

Uniform contact voltages within a cell are far more important than the absolute value of contact voltages. Average contact voltage impacts power costs, while the

variability determines current distribution. Uniform contact voltages are realised by having well maintained cathode plate hanger bar and intermediate busbar contacts.

The stripping machine washing system must incorporate contact cleaning for removal of organics, copper oxide and electrolyte salts. Modern machines have targeted contact cleaning systems using high-pressure hot water. Small quantities of sulphuric acid can be added to the wash water to aid removal of copper oxide and improve contact voltages.

Routine cleaning of the intermediate bars must also be undertaken. Contacts should be cleaned by scrubbing with dilute acid during anode changes, and by hosing during cathode harvests. More frequent wetting of the contact zones should be avoided because copper corrosion will result in variable contact voltages.

To avoid dripping electrolyte on contacts, the cranes can be fitted with drip trays. The trays should be fully engaged prior to travel.

Intermediate Bar Design

An important aspect of intermediate bar design their ease of cleaning. There should be no recesses or crevices that allow electrolyte to pool, or the resulting salts that accumulate will corrode cell-top furniture and hanger bars, leading to poor current distribution.

The conventional busbar system used is the Walker system (3), where electrode pairs within each cell are connected electrically in parallel. Intermediate bars between each cell allow equalization of current passing from one cell to the next. Intermediate bar contacts are generally of dog-bone or triangular profile, which provide a high-pressure point contact when used in conjunction with round-contact hanger bars.

Alternative designs have been developed that are aimed at overcoming the perceived shortfalls of the conventional busbars system.

Wet contact systems (developed Hibi Kyodo Smelting, Japan) was used for many years at Xstrata's refinery and gave clear benefits with regard to current distribution and power costs. However there was also a cost associated with increased corrosion of intermediate bars and hanger bar contacts, and high water inputs to the electrolyte (4).

Double contact systems have been promoted for improved current distribution. All like-electrodes (cathodes to cathodes and anodes to anodes) in each cell are connected via a secondary copper equalizer bar, providing an alternative electrical pathway between electrodes. This system has proven useful where the primary contact is compromised. While conceptually sound, there are issues relating to cleaning and maintaining currently offered systems.

Optibar have developed a Segmented Contact System (5), which is based on a similar principle to the original Whitehead system (6). Each cathode is electrically connected to an anode in the following cell, while each anode / cathode pair is insulated from the other electrodes (no intermediate distributor bar). It is claimed to improve current density dispersion, giving higher current efficiency, better cathode quality and less shorts.

Cathode Plate Internal Resistance

Internal plate resistance normally accounts for 8-10% of the overall cell voltage. The majority of cathode plate resistance occurs within the stainless steel 'free-board' zone between electrolyte solution line and the first copper plating. A much smaller resistance exists in the hanger bar itself.

The ISA PROCESS^{TM} electroplated hanger bar design makes use of this property to significantly reduce overall plate resistance, so lowering power consumption. The copper coating extends from the hanger bar, across the welded joint and partially down the blade. This minimises the high resistance path across the stainless steel. The latest ISA Cathode BR^{TM} plate extends the copper depth from 15mm to more than 50mm giving superior electrical performance.

Solid copper hanger bars incur much larger power losses through the high resistance path between solution line and hanger bar. This results in a significantly higher internal resistance than electro-plated designs.

Low internal resistance is important for minimising power consumption, however uniform current distribution requires uniform plate resistance from plate to plate within a cell. Therefore the electrical properties of the plates must be maintained over many years. The predominant cause of diminishing cathode plate electrical performance is the corrosion of the hanger bar to blade brazed joint that occurs in some plate designs. Since corrosion rates vary between plates, this results in variable current distribution within a cell, particularly when new plates are intermixed with older plates.

The electrical performance of electro-plated hanger bars is essentially unaffected by corrosion in refineries. This is evidenced by operations at Brixlegg, Olympic Dam and Copper Refineries, where plates have operated for 15 years to date without significant corrosion.

Measurement of Current Distribution

Routine measurement of current distribution and contact voltages should be undertaken. This provides a valuable measure of the capability of the overall system encompassing anode and cathode geometry, alignment accuracy and contact condition. Plate currents are measured by inserting a DC clamp meter through the lifting window closest to the contact. A scale-up factor is applied to individual measurements, to account

for the portion of current not measured at the window (scale up factor equals rectifier current divided by the sum of all measured currents within in a cell).

Cathode plate contact voltages are measured using a millivolt meter, then resistance calculated by Ohm's Law. Resistance is independent of current density so provides a better performance measure than contact voltage.

The measured plate currents should approximate a normal curve, with standard deviation ideally less than 10% of the average plate current, excluding shorts or open-circuits. Average plate contact resistance should ideally be less than 50 micro Ohms.
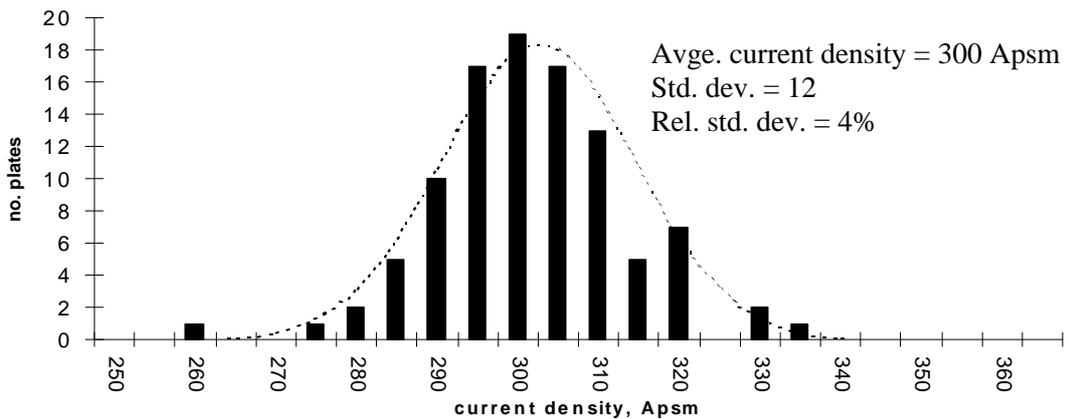

Figure 3 – Measured current distribution data, ISA PROCESS[TM] tankhouse (7)

Conclusion

The widespread introduction of the ISA PROCESS[TM] developed permanent stainless steel technology initiated a rapid increase in the intensity of the copper refining process. The superior and predictable verticality of permanent electrodes led to major improvements in current distribution and cathode quality, and increased intensity of operation.

Many refineries have benefited by achieving increased capacity of their plants at lower operating cost. The increased current densities being employed have required further improvements in the current distribution within cells and on cathode surfaces.

Improvements in anode preparation machinery and crane systems in conjunction with permanent stainless steel cathodes have further facilitated the improvement in electrode geometry. However the drive to reduce refining costs by increasing current density has caused greater emphasis on the ancillary components within the system. The need for a complete operating system with a key focus on the maintenance of current distribution is essential for production of high quality cathode demanded by the market place.

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