

CUMULATIVE DISTRIBUTIONS of METALLIC IMPURITIES

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Abstract

Concerns with metallic impurities in aluminium reduction cells are often focused on trend data that offers limited information. The study of the shape and variability of the overall distribution of all reduction cells often offers greater insight into issues with raw materials, process control, or factors such as air-burning that result in bi-modal or more complex distributions. In this paper the author offers insights into how to interpret this information. Conclusions are focused on the value of these interpretations as a tool to manage metal purity and to provide process feedback.

Introduction

Averages are most often used to track the progress of metallic impurities in pot room metal. This serves a few practical purposes. Measures of central tendency can quickly convey information on improvements or emerging issues. Average values for a specific metal impurity can be useful in tracking long term trends. They can also be used to make comparisons to impurity trends of a specific raw material.

However, as a measure of central tendency, averages are weak in their ability to rapidly identify emerging trends that affect only a sub-set of the population. Averages also become biased by any strong skew in the data. Causes of skew in a parent distribution may have little to do with factors that determine central tendency or typical performance. As an example; a few very high iron pots near the end of life may shift the average of a distribution even when the mode, or central point of the distribution, is unchanged.

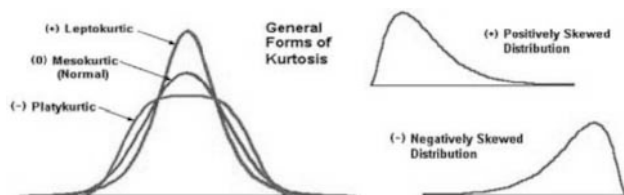


Figure 1 – Examples of various types of distributions [1]

Averages also fall short in communicating the kurtosis of a distribution [2]. In most cases a very tight, leptokurtic, distribution with little variation from pot-to-pot is preferred over a wide, platykurtic, distribution. But, each of these types of distributions may have the same average value. See figure #1. As Mr. Kerry Farmer, Smelting Manager of Alumax at Mt. Holly, S.C. once said during a presentation at a TMS annual meeting during the early 1990's; "Operating a smelter is an exercise in reducing variability." [3]

But, there are certain circumstances where skew in a distribution can add value. Such is the case with selective metal tapping to capture ingot that has certain purity or other characteristics.

In any situation the distribution of certain metallic impurities can come to define those products that a smelter is capable of producing. Understanding distributions of impurities and coming to know which factors commonly drive changes in shape and placement can also help pot line data to better communicate to the process engineer which changes are afoot and when.

Discussion – General Shape

Normal, Gaussian distributions of metallic impurities in aluminum from reduction cells are rare, or perhaps non-existent. Even, trace impurities such as Pb, Ca, and Co exhibit some of the same characteristics as more prevalent contaminants when it comes to the shape of the distribution. Refer to figure #2.

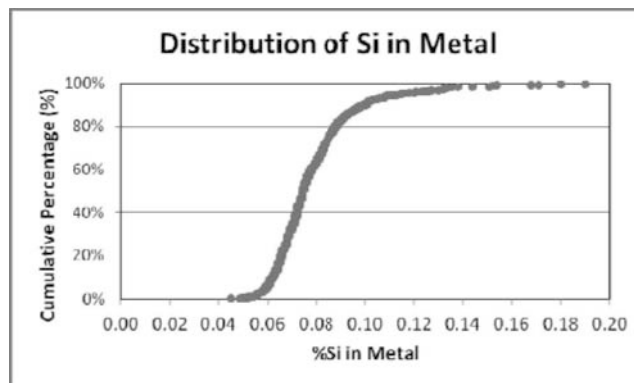


Figure 2 – Common distribution shape for metallic impurities

Common causes of variation affect all reductions cells. The degree to which common causes dominate the distribution is illustrated by the long, fairly straight, "slope" of the curve [4,5]. This is the most Gaussian fraction of the overall distribution. Even with trace impurities this section of the distribution seldom encompasses >90% of population. Refer to figure #3.

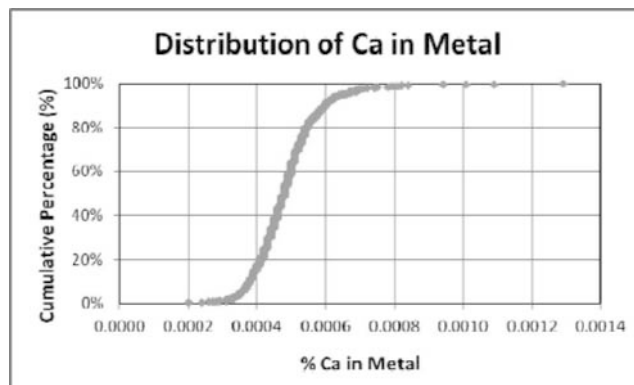


Figure 3 – Example of "slope" for a trace impurity

Slope provides a way to visualize kurtosis. A distribution with little variation will have a steep slope, as with a leptokurtic distribution. A slope that not as pronounced displays more variation from pot-to-pot and may also be platykurtic.

The other characteristic of a distribution that is tied to common cause variation is its “position”. Simply put, the sum of the inputs of many impurities, such as gallium will determine its position along the x-axis. When a raw material source changes, it is quite common that the position of the distribution of an impurity will shift to the left or to the right.

Then there are the sections of these distributions that are controlled more by special causes of variation. The impact on Fe in metal of a fallen anode, or burn-off, is one example. The “curvatures” at the top and bottom of distributions and the “tail” that is often found near the top of distributions are the realms of special causes of variability. The curvatures and tail provide a way to visualize the skew in the total population. While these zones appear to primarily represent the problem pots in a pot line, this is where the ability of the process to communicate what changes are afoot is often most powerful.

The general terms used going forward shall include: shape, slope, position, upper curvature, lower curvature and (upper) tail of the distributions that will be used as examples.

Discussion – Position

As noted above the most common way to change the position of a metal impurity distribution is to change a raw material. An example of this is given in figure #4.

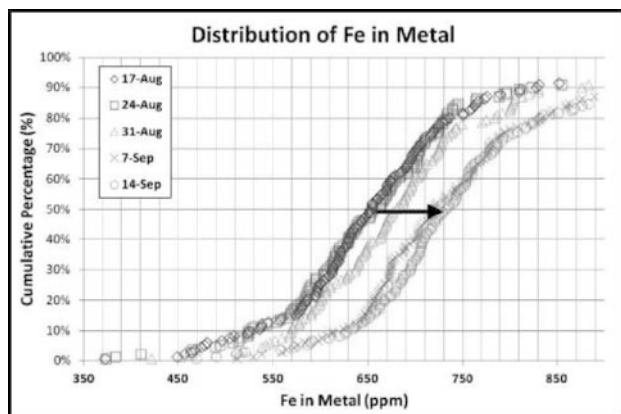


Figure 4 – Example of a change in position of an iron distribution

In this case two raw material inputs changed simultaneously. The net effect of these changes was to shift the position of the cumulative distribution curve ~80 ppm to the right. Note that there were no significant shifts in the shape of the distribution. Two common cause factors that uniformly affected all reduction cells was the only significant change.

This case study leads to an interesting observation. Changes in the position of a distribution can act as markers, or time stamps of when changes in raw materials arrive to a pot line. The example in figure #4 indicates that the shift began sometime between the 24th and the 31st of August.

If another change in pot line performance such as excessive carbon dust had its root cause as a raw material change, then a contaminant time stamp could help to properly assign cause. The shift in position may not always be related to iron, as in this case study. Other trace elements may be used to accurately follow the time lines of events.

Over the course of time the best trace element(s) to be used as markers may change. It may be Zn for alumina, Pb for pitch, Ni for coke, etc. This means that it can be useful to have a wide spectrum of analysis in quantometer measurements that are made on metal samples. The range of elements to be analyzed may need to extend beyond a short list of impurities that are of concern for a limited portfolio of metal products.

Then the question may arise; “What is the appropriate frequency of metal sampling?” The example shown in figure #4 is at weekly intervals. If there is a need to time stamp raw material changes with greater accuracy there are some options to consider. One can sample all pots more often. Or, the metal sampling plan can be adjusted so that not all metal samples are taken on the same day of the week. If the population of cells in a pot line or a plant is large, a sub-population can also deliver information on when changes in the position of a distribution occur.

Discussion – Slope

The examples given so far all have different slopes, or at least they appear to. The example of Ca in metal appears to be steep, and it is. The example for Fe appears to be a more gradual slope, and this is also correct. But, the way that these graphs are prepared and the choices made on how the data is presented can change the apparent slope of the distribution for a casual observer. A more rigorous definition is needed.

A rate of change metric is appropriate. In figure #4 this might be expressed as a change of +41 percentage points per +100 ppm Fe, or 41%/100 ppm. In the case of calcium in figure #3 this is closer to 41%/1 ppm. The rate of change per 100 ppm is most useful for major impurities such as Fe or Si. The rate of change per ppm is also useful, primarily for trace impurities. But, either measure helps to establish a uniform basis for comparisons.

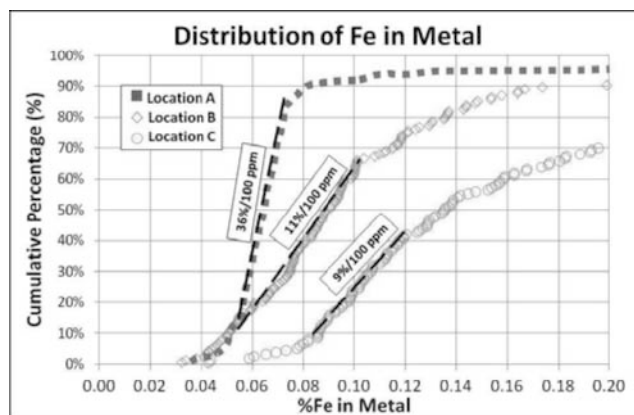


Figure 5 – Example of differences in slope

Figure #5 shows such a comparison and a wide range in the slopes of iron distributions from various locations and pot lines. Note that the slope for Location A in figure 5, at 36%/100 ppm, is not

quite as steep as the example that has been shared in figure #4, at 41%/100 ppm. But at first glance the example from figure 5 appears much steeper. The difference is with the x-axis scaling.

In most cases a steep, leptokurtic, slope, as is shown for Location A, is preferred. It is a sign of process health, or stability. With a multitude of factors in that can affect the %Fe and %Si in metal some locations have used slope metrics as an overall process stability indicator. In some circumstances this has been the case even when no products from the location required low levels of impurities. The goal was to drive those factors that improved slope and thus, operational stability.

A steep slope for impurities such as Fe and Si can enable greater yield of value-added metal grades such as those required for foundry, conductor rod, or high purity ingot. This is clearly the case for Location A versus Location B as illustrated in figure #5. The lower curvature of both cumulative distributions begin in the same place. But, Location A has much greater capability to produce quantities of metal that is lower in iron impurity.

As slope is a metric for common cause variation, differences in slope are driven by factors that can randomly affect reduction cells. In the case of Fe these include:

- Total liquid level
- Bath level
- Anode butt thickness
- Work practices
- Raw material variability
- Sodium oxide level in alumina

The most powerful of these factors are bath level targets and control of liquid levels and/or the average thickness of anode butts and variation in thickness. Refer to figure #6.

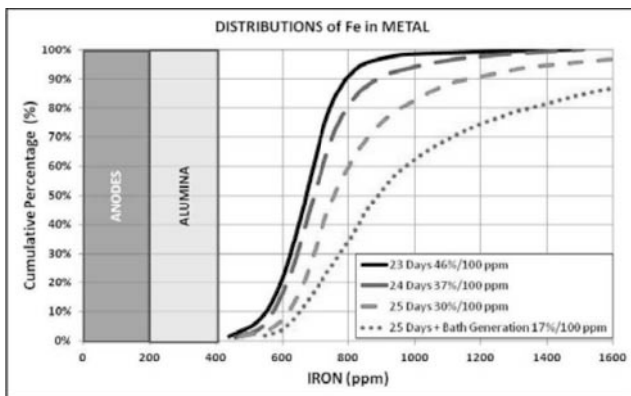


Figure 6 – Impact of anode life and bath level upon slope

Figure #6 shows the results of a comparative study of various anode changing cycles plus the impact of intentional bath generation in combination with one of these cycles. The impact upon slope is impressive. A range of 46%/100 ppm Fe down to 17%/100 ppm Fe is observed in the results. It is quite clear that the common factor in this situation is the chance of liquid bath making contact with castings around the anode stubs.

Thus, when a change in position of the distribution is observed it is best to look to raw materials. When a change in slope is observed it is best to look to factors that are related to common process variables.

Tracking the slope of impurity distributions over time offers the ability to establish control limits and reaction plans on these factors that can affect metal grades. In some cases, such as with bath or total liquid levels, this may be redundant. In other cases a significant shift in slope may serve as a clear sign to consider other actions such as changes in the anode setting cycle.

Discussion – Upper Tail

The upper tail of a distribution for a metallic impurity is actually a misnomer. Refer to figure #7. It appears to be a rather extreme version of a positively skewed distribution. In one sense the upper tail may be considered as a sub-set of an overall population of reduction cells being acted on by a special cause. Such is the case with cells that are very high in iron content. This is typically caused by contact of the metal pad with the collector bars of the cathode and the castings that surround them.

It may also be argued that such cells belong to a different population entirely as they share a different cause that is common to each of these reduction cells, but not the rest of the population. In fact, many of the examples shared here have this portion of the distribution truncated to allow for more accurate visualization and analysis of the major fractions of the cumulative distributions.

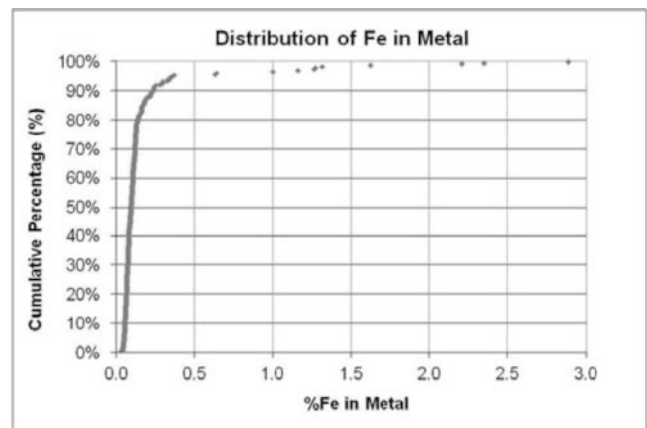


Figure 7 – Example of an iron distribution with an upper tail

Upper tails for metallic impurities in aluminum from primary reduction cells are usually limited to those contaminants that may be easily dissolved or consumed by molten bath. This list includes; iron castings, silicon from SiC sidewalls, items of cast iron or steel used to service pot operations, or items that may fall into the pot on occasion.

Upper tails may also be observed for contaminants such as Mn, Cu, and Cr that may be found in castings around anode stubs or castings such as gas manifolds for Søderberg cells. They may even be observed to some extent on trace impurities as with the example shared in figure #3 on %Ca in aluminum.

The information that this portion of the cumulative distribution offers is often the least useful. It can demonstrate how metal from a very few reduction cells can have a profound impact on the average value for an impurity. But, it offers little in the way of important insight or feedback from the process except to highlight how many cells are suffering an extreme impact of a special cause of variation that is generally well understood.

Discussion – Upper and Lower Curvature

As with the slope of the cumulative distribution the areas that have been defined as the upper and lower curvature can be quite telling as to what is happening in the process at any given time. In the case of figure #8 we can observe that approximately 25% of the pots are higher than we might expect for Cr content.

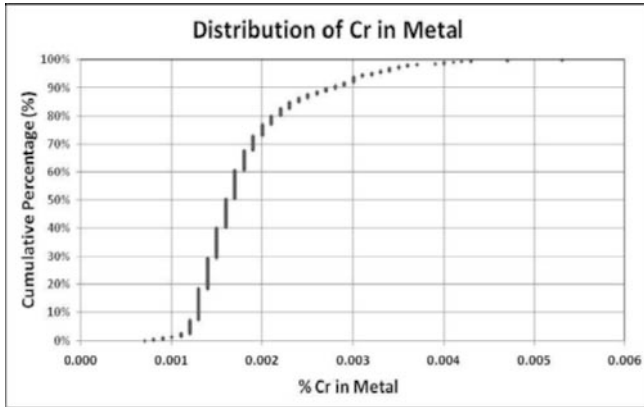


Figure 8 – Example of curvature in distribution of Cr in metal

In this particular case there had been some delays in the regular schedule of anode changing and roughly 25% of the pots were encountering some attack on steel components of anode rods that had chromium in its composition. Thus it became possible to use this data to confirm the degree of impact and plan for repair rates accordingly.

In some cases a special cause of variation becomes common enough that a secondary slope, or bi-modal distribution, can be clearly observed. Refer to figure #9.

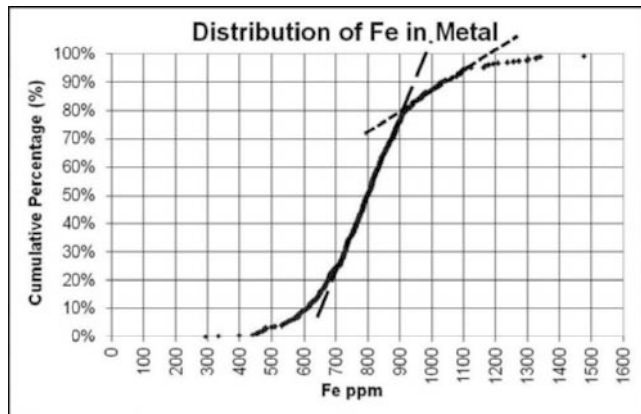


Figure 9 – Example of a bi-modal distribution

In this particular case the anode bonnet design and the proximity of iron castings to point feeders caused a predictable and repeatable amount of air burning around specific castings. Approximately 15% of the overall population showed castings that had been exposed by air burning to also have been attacked in various degrees by liquid bath.

Normally the upper curvature, or range between the slope of the curve and the upper tail, is the realm of exception pots. These may be unusually hot, high in superheat, or difficult to control.

These pots may also include; anodes that have air-burned and exposed iron castings, cells with recent burn-offs, or pots with intentionally high bath levels that are used to support new pot starts. They are also often good matches for the exception lists that pot line coordinators work from on a daily basis.

The size of the upper tail is another measure of process health. In the case of figure #9 approximately 15% of the population is in this zone. Examination of other the examples in this paper show that this may be as low as 10% of the population or greater than 20%. Tracking the magnitude of the upper curvature over time can give insight on the degree of health of a pot line or plant. It captures at any given time that fraction of the total population that may not be producing well. Thus, it can serve as an objective measure based on data more than opinion.

The lower curvature of a distribution is another form of exception pots. From the examples shared here we can see that between 3% and 10% of pots typically fall into this zone. Pots that expel carbon dust to the fume control system have been observed to also carry away significant amounts of metallic impurities [6]. Cells that generate excessive amounts of dust that is removed either by this means or by skimming generally define the lower curvature of the distribution. Thus, this is generally in the realm of anode quality and may even serve as a secondary and pot room specific metric of anode quality.

Conclusions

Cumulative distributions for metallic impurities can offer a wealth of information. They provide a more holistic view of a pot line, reduction facility or groups of reduction cells than average values can provide. They can be used to visualize kurtosis and skew and apply this information to better understanding or confirmation of what is actually happening in the process.

These distributions can be broken down into elements that may also be used as process health metrics. Common causes of variation can yield measures of position and slope of the distribution. Time series analysis of changes in these metrics can give insights into raw materials and process factors such as anode butt thickness and bath level control.

The special causes of variation that are assigned to the curvatures and upper tail of such distributions can also yield information on process health and changes to it that may be observed over time.

Specific insights may be gained on a variety of sub-processes.

Tracking of specific, trace impurities may also be used as markers to time-stamp when a shift in raw materials was actually realized in a pot line.

Plotting such distributions and the distribution-metrics that have been discussed in this paper can give process control personnel data-based insights or confirmations as to what is actually happening to a group of reduction cells and when.

References

1. Examples of kurtosis & skew by MVP Programs, 2007, <http://mvpprograms.com/help/mvpstats/distributions/SkewnessKurtosis>

2. Box, George, E. P, Hunter, William G, Hunter, J. Stuart, “Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building”, 1978, John Wiley & Sons, p. 90
3. Farmer, Kerry, Alumax of South Caroline, quotation from TMS annual meeting, 1990’s, exact year unknown
4. Lindsay, S. “Bridging the Gap Between Refineries and Smelters”, 8th Australasian Smelting Technology Conference, 2004, 148-162
5. Lindsay, S. “Diagnosing Iron Contamination in Pot Room Metal”, Light Metals 2005, 393-397
6. Gaertner, Heiko, Ratviki, Arne Petter, & Aarhaug, Thor Anders, “Impurity Elements in Raw Gas Ultra-Fines from Aluminium Electrolysis Cells”, Light Metals 2012, pp. 839 – 844

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