CURRENT EFFICIENCY IN PREBAKE AND SØDERBERG CELLS

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Abstract

An isotope dilution technique was used to study 24 h current efficiencies in 22 semi-randomly selected prebake pots and 21 randomly selected Søderberg pots at the Elkem smelters. A total of 110 measurements were made and compared with the 1128 current efficiency measurements made on Alcoa prebake pots using Alcoa's silver dilution technique. Results are discussed with emphasis on similarities and dissimilarities in prebake and Søderberg pots. Some theoretical proposals are made regarding the similarities and differences.

Results for the prebake pots confirm the basic conclusions from the Alcoa studies including the relative importance of bath chemistry compared to noise (instability) and the impact of low alumina operation on current efficiency. Measurements of 24 h current efficiencies for Søderberg pots are scarce to non-existent. Only temperature and aluminium fluoride have similar influences in the two pot technologies.

Introduction

Elkem initiated in 2002 a series of short-term (24 h) current efficiency measurements in their smelter at Lista (EAL), later extended to the Mosjøen (EAM) smelter. The smelters operate point-fed Søderberg and prebake pots, respectively. The technique chosen was radiotracer dilution. Measurements are still in progress.

Present data permits a direct comparison of Søderberg and prebake current efficiencies, measured using an identical technique. Short-term measurements of current efficiencies with dilution techniques appear not to have been applied to Søderberg pots before. Particular attention was paid to the effect of alumina in modern point-fed Søderbergs [1].

Prebake pots have been subjected to a closer scrutiny than Søderbergs. Alcoa has at its disposal a large database comprising 1128 short-term current efficiencies in prebake pots, measured with their silver dilution technique (SDT). Results are compared with conclusions drawn from a much smaller body of 110 Elkem radiotracer measurements.

Experimental techniques

Silver dilution technique

The basics of the Alcoa SDT has been described previously [2]. The following improvements have been initiated since the first description of the procedure. A eutectic alloy of 70% Ag and 30%

Al with a melting point of 596 C is used to introduce the Ag to the pot. The low melting alloy assures the Ag does not get lost in muck or bottom deposits.

The precision of the analysis technique has been improved and a built-in test developed to determine if any of the Ag has been lost in muck or isolated pools of metal. Figure 1 shows a fairly typical example on a single pot. The overall average current efficiency for the period was measured at 96.5% with a starting inventory of 7921 lbs and an error in the current efficiency (as determined by the std error of the slope) of 1.4%. Although the error of 1.4% appears to be quite high this error is due to two factors. First, real changes in current efficiency as a result of a process shift. Second, errors due to technique inadequacies (metal injection, sampling and analysis).
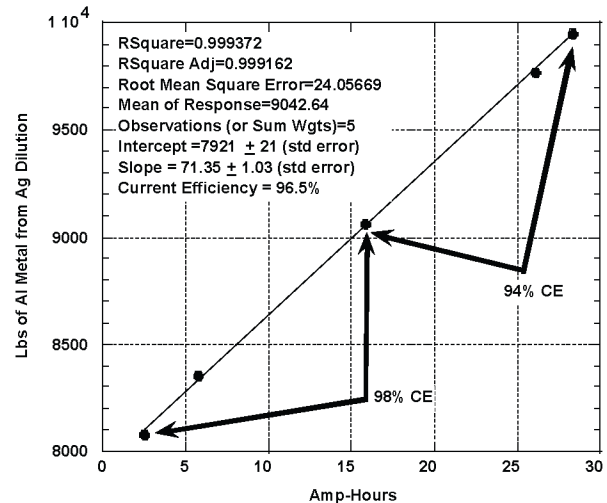

Figure 1. Example of current efficiency measurement using the SDT technique at Warrick (Pot54).

Notice the dilution slope (current efficiency) is higher during the first part of the test than the second half of the test. This is, as shown in Figure 2, a common occurrence that we attribute to a decrease caused by the upset of setting the pot. Reported errors in the slope are due to both this upset (which we attribute to a real process upset) and the inherent metal injection sampling and measurement errors (i.e., technique errors not related to the process).

The technique errors can be detected a fair amount of the time. The measurement capability is also dependent upon the pot design and the measurement ability. The pot design matters because the

inherent metal inventory and relative amount of metal tapped set the relative precision.
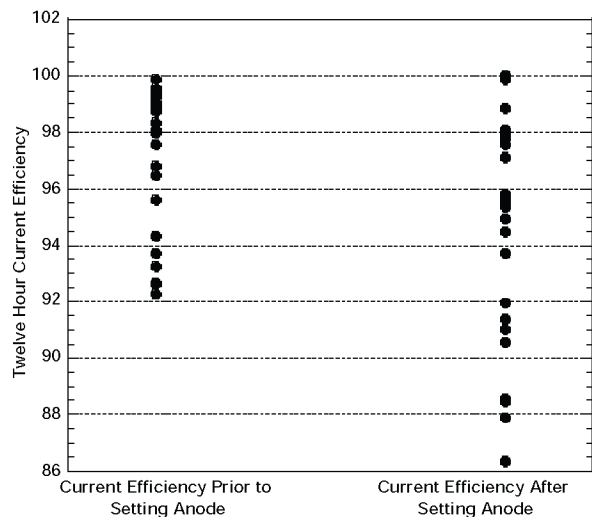

Figure 2. Current efficiency prior to and after anode setting (SDT)

This built-in correlation allows us to detect most out of control technique errors, as shown graphically in Figure 3. The possible errors due to a metal injection, sample or analysis problem will be at the fringes of the scatter plot. We certainly would not be justified to eliminate any of the data that is within the expected spread.
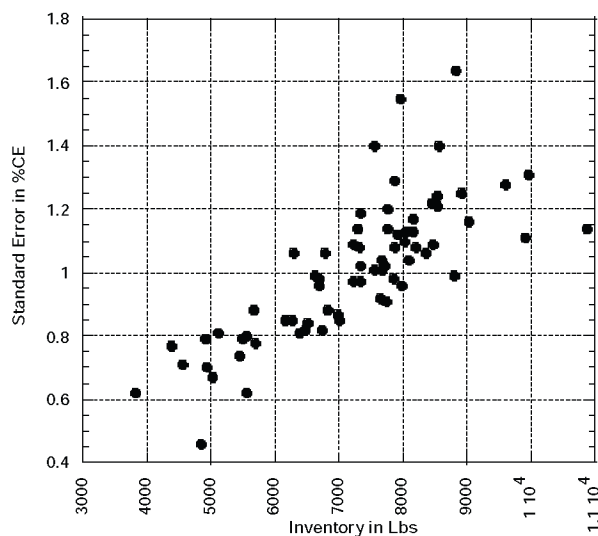

Figure 3. P-100 metal dilution current efficiency (SDT). Standard error of slope vs. aluminium inventory

Radiotracer dilution technique

The radiotracer dilution method used by Elkem was developed by the then Institute of Inorganic Chemistry at the Norwegian Institute of Technology in Trondheim, Norway [3,4,5]. The major modification made to the method by Elkem has been to replace the radioactive gold tracer (Au-198) with radioactive gallium (Ga-

72) having a half-life of only 14 hours. Irradiated Al3%Ga "pills" weighing only 3 g are used, facilitating introduction to the metal pool only. Due to the rapid decay, all work has to be completed within about 36 hours of receiving the radioactive material.

An example is given in Figure 4 for a Søderberg pot containing on the average 9.7 metric tons of metal and producing 870 kg per 24 h. The standard error (SE) in the current efficiency is 0.7%.
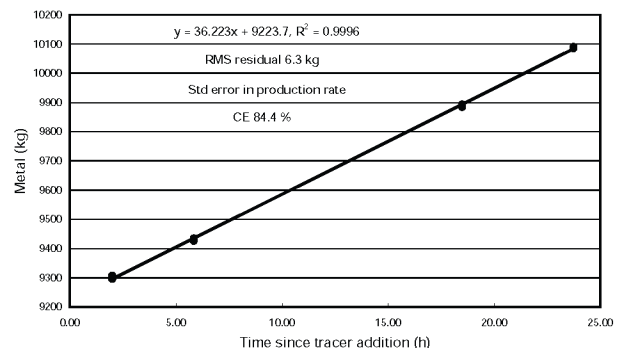

Figure 4. Radiotracer dilution example at Lista (two points at each time). Low CE 84.4% is due to anode problems.

Ga-72 emits gamma radiation that penetrates about 60 mm of aluminium before the intensity is reduced by 50%, and the 12 mm radius cylindrical samples are counted in a well-type detector. The detrimental effect of tracer segregation is thus largely nullified (care is taken not to remove any metal from the sample surface prior to counting for the same reason). Pots can be remeasured after only 5 days. The present Elkem routine is to measure current efficiencies in 20 pots per week, and these may be the same 20 pots. Current efficiencies are output immediately. Pot data and bath samples are gathered at about 3 h intervals during the 24 h measuring period.

The current experimental procedure is to take four metal samples about two hours after tracer addition, and another set of four samples just before the next tapping. The accuracy is for statistical reasons reduced by a factor of about 2 [6] compared to sampling at evenly spaced intervals.

A comparison of methods
With the SDT method, inventories are determined with an SE of 10-100 kg and the current efficiency with 0.4-2%, both depending on the inventory. The SE in the inventory is 0.06-0.13% with the radiotracer method, corresponding, for example, to 5-10 kg at 8 metric tons of and 1% in current efficiency if the production rate is 1.1 ton/24h. Neither method has customer impact. Regulatory training is required for the radiotracer method, not for SDT. Pots can be retested after approximately 30 days with SDT depending on dilution rate, and in 5 days with radiotracers. Current efficiencies await later analysis of samples with the SDT metod. They are immediately available with the radiotracer method, as samples are counted on site. Outliers are detected in both methods.

Pot selection

In Mosjøen 22 prebake pots were selected semi-randomly. About 10% were deselected on the basis of process computer reports, known operational problems or age (very young pots). A total of

55 measurements were carried out, of which 41 were on pots in ordinary operation and 14 on pots in a controlled alumina concentration experiment. At Lista, 21 pots were selected completely at random. All pots were in ordinary operation. The total number of current efficiency measurements was 55.

The Alcoa routine for selecting pots is essentially identical to Elkem's in Mosjøen. Alcoa also makes sure prior to the test that most of the critical parameters (chemistry, temperature, noise, superheat and power input) in the selected sample mirror the overall population. This usually means eliminating very young pots, pots at the end of the line with known magnetic problems and special test pots (usually cathode design trials) that may just happen to be part of the plant's population.

Controlled alumina experiments with radiotracer

The radiotracer technique is particularly suited to controlled experiments, in which variables are deliberately altered and the response in current efficiencies determined. This is because the pots can be retested within 5 days, thus reducing pot biases.

Ten Mosjøen prebake pots in stable operation were selected and arbitrarily divided into two groups. In the first week of the study, one group was left in ordinary operation. The other was subjected to forced alumina feeding, starting the day before 24 h measurements commenced in both groups. Alumina feeding was returned to normal after measurements. One week later the experiment was repeated, this time with forced alumina feeding taking place in the other group.

Results

An overview is given in Table I, where SB is Søderberg and PB prebake pots.

Elkem radiotracer results

All terms in the fitted multiregression models below are significant on the 5% probability level, or better. Variables with higher p-values were rejected. EAM are prebake models for Mosjøen, EAL Søderberg models at Lista.

EAM Model 1
CE =235.1-0.1470*Temp+1.552*(alumina-2.533)
(AlF3-12.478)+0.254(alumina-2.533)*(Temp-957.046)
Residual error 2.21 CE%

EAM Model 2
CE=289.2-1.39*alumina-0.723*Metalheight
-0.190*Temp
Residual error 2.30 CE%

EAM Model 3
CE=102.3-424*Cal
Residual error 2.53 CE%

EAL Model 1
CE =76.2+0.919*AlF3-0.0107*(Total height-46.418)
*(Bubble noise-89.407)+1.39*Feed curve points
Residual error 2.58 CE%

Variable names have their usual meaning, with units given in Table I. Cal in EAM Model 3 is the "metal" solubility as calculated by an updated version of Wang et al. [7] solubilities. Lista has recently split pot noise into two components, MHD noise and bubble noise. Bubble noise appears in EAL Model 1. Not included in Table I are Feed curve points in the same model, an evaluation graded from 1 (bad) to 3 (OK) with a mean of 2.0.

Forced alumina feeding in the controlled experiment had no significant effect on temperature and acidity, in line with other observations in pots in ordinary production. Mean temperatures for all pots were 951 C first week and 948 C second week. The mean increase in alumina first week in the group of 5 pots with forced feeding was 1.45%, the next week 0.84%. The corresponding decrease in current efficiency was 2.0% and 2.4%, respectively. The mean increase in alumina concentrations for the ten pots that were force-fed was 1.14%, the mean decrease in CE 2.33%. Thus, the mean decrease in current efficiency for a 1% increase in alumina concentration is 2.0%.

Discussion

Elkem

The metal height effect in EAM Model 2 is weak. The alumina and temperature coefficients are the important terms in this model. An EAM model with only superheats calculated from the phase diagram of Solheim et al. [8] had a residual error of 2.9%. The metal solubility model EAM Model 3 based on Wang solubilities has the best fit of any single-parameter model. EAM Models 1 and 2 are considered the best descriptions of current efficiencies in Mosjøen prebake pots.

Below are listed current efficiencies, directly observed coefficients (bivariate plots) for temperature and excess AlF$_3$, and alumina coefficients found from EAM Model 2 and the controlled alumina experiment. No model was found for Søderberg pots in which the alumina content emerged as a significant variable.

	PB	SB
Temperature, %CE/C	-0.19	-0.17
Excess AlF$_3$, %CE/%AlF$_3$	0.56	1.35
Alumina, from models, %CE/%Al$_2$O$_3$	-1.39	(-)
Alumina, controlled experiment	-2.0	(-)
Excess AlF$_3$ vs temp, %AlF$_3$/C	-0.17	-0.12
Max CE, %	98	96
Peak CE, %	96.5	91
Mean CE, %	94.4	90.5

The loss in current efficiency resulting from a skewed efficiency distribution is simply equal to the difference between the peak value and the mean value. The basic assumption is that pots on the high efficiency side are not significantly affected by the factor(s) responsible for a tail of low-yield pots. From the table above the loss is 0.5% for Søderberg pots at EAL. In an earlier period with extreme anode problems at EAL the difference was 2.8%, and the calculated efficiency increase since then hence 2.3%. The actual improvement is 2.1% according to plant data. It may also be noted that peak and maximum values for current efficiencies were nearly the same both times, supporting the basic assumption.

Table I. Overview of Results Comprising 1128 Alcoa and 110 Elkem Measurements

Variable	SB Range	SB Mean	PB range	PB Mean	Alcoa Range	Alcoa Mean
Current Efficiency, %	82.9-96.2	90.5	85.9-98.3	94.4	18.75-99.79	93.9
Temperature, C	948-984	965.5	940-985	957	923-1035	961
Excess AlF$_3$, %	6.9-14.8	10.8	6.8-17.0	12.5	5.2-16.6	10.5
Alumina, % *)	2.62-6.51	4.0	1.50-4.20	2.49	1.42-10.6	3.32
CaF$_2$, %	2.9-6.5	5.3	5.67-6.41	6.0	4.3-6.5	5.5
Metal Height, cm	18.4-25.4	21.4	10.6-16.4	12.7		
Metal Inventory, kg	7723-12755	10507	5679-10802	8532	712-23623	4814
Bath Height, cm	18.1-34.9	25.0	15.8-29.3	22.6		
Pot Voltage, V	4.68-5.12	4.86	4.33-4.85	4.57	3.98-5.20	4.48
Pot Amperage, kA	126	126	161	161	70-322	155
Calculated Superheat, C	2-21.7	12.5	0.5-28.9	15.8	0.6-103.2	8.94
Calc. Met. Solubility, %	0.015-0.033	0.022	0.013-0.032	0.0186	0.009-0.17	0.037
Anode Current Balance **)					5.0-48.2	16.97
Instability (noise), μΩ	42-162 ***)	89 ***)	0.179-0.612	0.280	0.06-3.8	0.3

*) PB alumina analysis results are systematically 1% low relative SB. **) Std.Dev/avg, %. ***) Bubble noise, mV.

For prebakes in Mosjøen the potential gain in efficiency is 2.1% if low-yield pots, in this case hot pots, can be eliminated to give a symmetrical, normal distribution. Both current efficiency and temperature are, unlike at EAL, strongly skewed. See Figure 5.
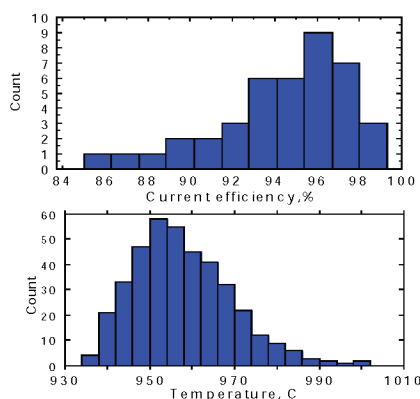

Figure 5. Current efficiency and temperature EAM

The temperature coefficient for prebakes is identical to the figure –0.19 %CE/C arrived at by Kvande [9] from temperature coefficients reported up to 1989. The value -0.17 for Søderbergs is close and probably within error limits. The temperature effect appears not to be cell dependent.

The much larger body of experimental data collected for prebakes by Alcoa shows that the temperature effect is non-linear, with current efficiency vs. temperature slopes ranging from -0.5 %CE/C above 980 C to zero at about 950 C where a maximum in the current efficiency occurs. The mean temperature coefficient is -0.19 %CE/C for the temperature ranges in the present Elkem work for prebakes and Søderbergs, in agreement with the above value.

Kvande's literature survey concluded that the effect of acidity on current efficiencies is in the range 0.4-0.71 %CE per percent excess AlF$_3$. Particular emphasis was put on the Lewis [10] value of 0.56, which happens to be identical with ours for prebake pots. Berge et al. [3] has reported a coeffficient of 0.59 found by a technique similar to the present.

The AlF$_3$ effect found for Søderberg pots, 1.35 %CE/%AlF$_3$, is about twice the prebake value. The effect may thus be somewhat cell dependent, but temperature and acidity are both important to current losses in both technologies.

There is a strong correlation between AlF3 and temperature in both types of pot. The coefficients -0.17 and -0.12 %AlF$_3$/C in the text table above are based on means of 9 measurements/24 h, R^2 being 0.66 and 0.40 for PB and SB, respectively. They are compatible with the liquidus temperatures of Solheim at al. (no significant correlation with temperature was found for alumina). The correlation presents serious orthogonality problems in modelling; including both terms explicitly unfortunately weakens the reliability of both coefficients. It is better to choose one, letting it include the influence on the current efficiency of the other. In practice, the same strong correlation makes for no real need to separate the effects. The -0.19 %CE/C coefficient above thus includes the effect of AlF$_3$.

Comparison with literature claims concerning the effect of alumina on prebake pots (e.g., Solli et al. [11]) can briefly be summarized as follows:

- Alcoa's SDT results with 1-3% decrease in CE per 1 wt% alumina in prebake pots are validated. Alcoa's low-alumina strategy in process control is correct.
- The oxygen balance method of Leroy et al. [12] in a prebake pot (1.5-3.2% alumina) is validated. Aluminium Pechiney's long-standing claim that CE increases with decreasing alumina content in prebake pots is correct.
- Alumina effects derived from CO_2/CO gas analysis are wrong.
- Literature suggestions that the alumina effect is cell dependent are correct.

It is proposed here that the relatively low current efficiencies in Søderbergs and the insensitivity to alumina both may be due to geometry effects. Metal solubility models predict that current efficiencies should increase with increasing alumina contents. Observations to the contrary are generally explained by another and opposing alumina effect, namely, the influence of alumina on the bubble area and therefore recombination reactions. The longer travel under the large Søderberg anode gives bubbles more chance to coalesce and grow bigger as well as producing more noise (the

structure of the anode surface is another factor) [e.g., 13]. This geometry effect on the bubble size may dominate over the alumina effect. In other words, efficiencies in Søderbergs are relatively low due to the large size of bubbles escaping from the large anode, and they stay low independent of the alumina concentration for the same reason.

Another explanation for the missing effect of alumina on Søderberg current efficiencies is suggested later, from Alcoa observations. A common denominator for both similarities and dissimilarities in prebakes and Søderbergs may simply be the solubility of metal in the bath: Temperature and acidity have similar effects on the current efficiency because they are prime movers of metal solubilities, and the dissimilar effects of alumina can be caused by secondary factors that disrupt or overshadow the alumina effect on the metal solubility.

Alcoa

Operating a potroom is an exercise in minimizing variation while balancing often conflicting decisions. Pots operating at the extremes, high temperatures, high noise and "mucky" cathodes, are obviously not operating efficiently. Less clear is the trade-off between lower temperatures enabled by higher acidity and lower noise enabled by lower acidities. It is also not clear what types of work practices are important. For example, is a labor-consuming, very controlled anode balance really required or does the anode burn-back make the process inherently self correcting. Several key questions addressed were:

- How do we quickly identify pots that are not operating efficiently?
- How do we decide between the trade off between low noise operation and a low temperature operation?
- Can we predict current efficiency on a pot by pot day to day basis?

Alcoa has measured current efficiency since 1988 [2] to address these questions, the overall goal being to identify which routinely measured pot parameters had the greatest impact on current efficiency. Strategies and guidelines to optimize current efficiency have been described [14-17].

The following empirical model based upon 1128 measurements can be used as a guide to answer the questions above:

% CE = 103.68 -134.85*Cal -50.438(% alumina-3.463)*(Cal-0.0357) − 0.969*% alumina -1.192*noise − 0.0638*%Anode balance + 0.0978*(%Anode balance-17.719)*(noise-0.3815)

%CE: Calculated % current efficiency, %
Cal: Solubility of "Al metal" in bath as described by Wang [7], %
% alumina: Average alumina dissolved in the bath, %
Noise: Maximum Resistance – Minimum resistance measured at the predominate metal pad roll period (30 seconds for smaller pots, 60 seconds for larger pots)
% Anode Balance: (Standard deviation of the anode rod current readings/Average anode current reading) * 100

The uncertainty of the models predictive ability can be used to assess the risk associated with a change in strategy or tactics employed by a potline supervisor.

The formula gives a residual error of 2.19% CE with an R2 of 0.70. A plot of the fit for this equation vs actual current efficiency is shown in Figure 6.
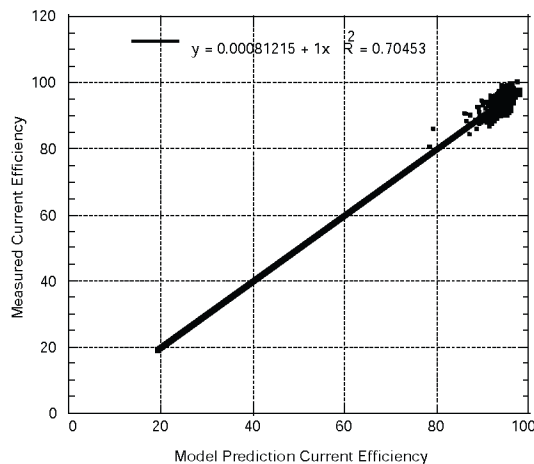

Figure 6. Measured current efficiency vs. model current efficiency.

The model was developed with a large database that inherently has a large range for the pertinent variables. The range is large enough that it covers the entire operational range of interest as shown below. Quantile percentages are given.

	Mean	SD	99.5%	0.5%
Ratio	1.13	0.054	1.28	1.00
Temperature	961	11.2	998	923
C*al	0.037	0.015	0.0105	0.013
Alumina	3.42	0.87	6.82	1.68
Noise	0.30	0.29	1.66	0.06
Anode balance	17	7.25	43.7	5.00

The large range for each variable can be used to establish a relative importance to each by normalizing each data set to an equal range. The Pareto chart Figure 7 shows the relationship between the various factors in the model, indicating that C*al (which is driven by low temperatures and low ratios) is nearly twice as important over the range of data as any of the other factors.
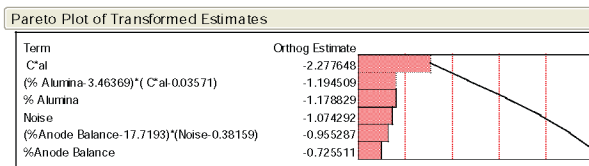

Figure 7. Relative importance of terms in Alcoa model.

This is a linear estimate, and all the factors may not be linear. Nevertheless, to a first approximation a pot is better off operating 1 C lower in temperature even at the expence of stability. If the increased noise, however, leads to a degradation of alumina control to the extent that the pot has to run 0.2% higher in alumina then the trade-off will not be worthwhile.

The model also points out that lower alumina concentrations are desirable. But, this advantage all but disappears at low C*al (low temperatures and ratios). Figure 8 shows why.
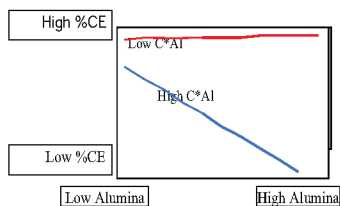

Figure 8. Current efficiency and alumina concentration.

At very low C*al the influence of alumina on current efficiency all but disappears. These very low values are in reality not achievable above 920 C and a 1.0 ratio. At normal conditions alumina concentration does make a difference, but sometimes so small that it is difficult to detect with a small sample size or too small changes in the alumina concentration.

The evidence now seems to be clear that alumina concentration in commercial pots does make a difference in the efficiency at which prebake pots run. The question is why the same effect is not apparent in Søderberg pots and laboratory pots. One explanation is that the superheat operation at low relative superheat helps to form a frozen layer of low acidity bath at the bath metal interface. This frozen layer prevents the reduced species from entering the bath and participating in the back reaction.

Figure 9 shows actual measurements of superheat and alumina taken during one of the silver dilution tests. Notice the general tendency for the superheat to be lower as the alumina concentration becomes lower.
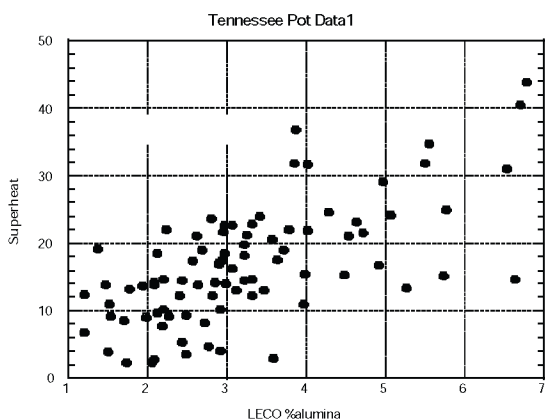

Figure 9. Superheat vs. LECO % alumina.

Clearly this superheat phenomenon would not occur in an externally heated laboratory pot. The reason it is not seen in a point fed Søderberg pot is less clear, but may be caused by the feeding taking place closer to the side walls than in most prebake pots, making for a thinner frozen layer. The change in bubble size with respect to anode area and alumina concentration is the other plausible explanation. This explanation seems likely for the

Søderberg vs prebake case, but is less satisfying for the laboratory vs. prebake example.

The silver dilution and radiotracer work both show that the biggest effort should be towards operating pots at lower temperatures with a most likely optimum around 950 C.

The following guidance has come as a result of this work. Each 1 C lower in temperature resulting from a higher acidity operation results in a 0.19% increase in current efficieny. The trade-off for a break even situation is a 0.026 increase in noise, or 0.10% increase in the average alumina concentration, or a 1.75% in anode balance (due to a necessary squeezing of the ACD to have a net zero change in energy input).

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