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Variability Analysis of Total Fluoride Concentrations from Two Reduction Cell Technologies in a Primary Aluminum Smelter

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Abstract

The Aluar Aluminum Primary Aluminium Smelter is composed of two potlines with Aluar cell technology (400 pots PFPB type at 200 kA) and two potlines with AP18 cell technology (384 pots PFPB type at 220 kA). Sampling of roof emissions is done with a 32 cassette arrangement according to EPA14A method for total fluoride (gaseous and particulate phase) emission control and monitoring. Following the guidelines of the methodology the cassettes are placed along the roof monitor of the 8 potrooms that form the 4 potlines.
From a total of 1651 values of total fluoride concentrations (822 for Aluar type potlines and 829 for the Pechiney type potlines) obtained from monthly measurements from September 2012 to May 2014, several statistics analysis were made in order to study the variability of fluoride emission in both technologies. The effect on the results of the run time sampling period was examined (24, 32 and 40 hours), which concluded that there were no significant differences were found between periods. In order to optimize our resources, the feasibility to alternate sampling between potrooms and its impact on long term fluoride specific emissions was also investigated for each type of potlines. Also enabled us to validate a recognizable correlation between pot hooding quality and fluoride emissions, which is presented is a separate 2015 TMS paper.

Introduction

The Aluar aluminium smelter is located in the Province of Chubut, just 2 km north of the City of Puerto Madryn. This is an environmentally sensitive area of the Atlantic Argentinian Coast that is characterized by flagship species of marine mammals like the Southern Right Whale.
Aluar started in 1974 originally with Montecatini SWPB 400 pots placed in two electrical potlines, each one with two potrooms of 100 pots each (Potline A: Potrooms 1 and 2, Potline B: Potrooms 3 and 4), operating at 150 kA. In 1987 pots were modified to PFPB technology and dry alumina type Gas Treatment Centers were installed. These improvements among others enable the pot to currently operate at 200 kA with good current efficiency [1].
In 1999 Aluar increased its production by adding 144 AP18 pots that later were upgraded to AP22 (Potline C: Potrooms 5 and 6), and finally between 2007 and 2010 Aluar concluded a further expansion with another 240 AP22 pots in two potrooms (Potline D: Potrooms 7 and 8). See Figure 1.

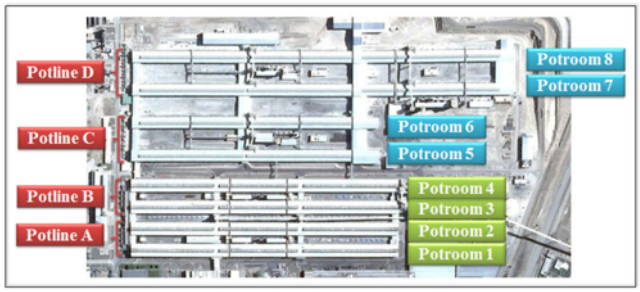

Figure 1 – Aluar Potlines Distribution

Total fluoride emissions (gas + particulate phase expressed as Ft) is a significant aspect of the primary aluminum smelter. The government through the Local Authority has established a series of regulations in order to control the plant's environmental performance.

The Ft emission limit enforced by the local authority is 1 kg Ft per metric ton of aluminum produced. This plant wide limit is distributed over all the sources in the plant: 84% corresponding to potroom roof monitor emissions, 10% to Gas Treatment Centers (GTC), 5% to Anode Baking Furnaces Fume Treatment Centers (FTC) and 1 % to Dross Processing Furnace Filters.

Sampling Method

Total Fluoride emission determination is carried out by USEPA 14a method for Potlines and USEPA 13a for stacks of GTC, FTC and filters. These methods have been developed and performed since July 2012 and a great amount of data has been collected since the methods have been applied.

USEPA 14a methodology establishes a location and then the placement of a minimum of 8 cassette arrangements strategically located at equal intervals across the roof of an electrical potline (4 cassettes per potroom) thereby covering at least 8% of the total length. Each cassette arrangement consists of a 0.8 µm cellulose filter and support pad in the first section for solid fluoride retention, followed by two 5 µm cellulose filters and support pads previously impregnated in sodium formate for gaseous fluoride retention through sodium reaction [2].

Fluoride mass determination and gas sample volume allows us to calculate the Ft concentration in the gas released into the atmosphere. The method stipulates that all the cassettes have to be connected by tubing to a manifold followed by a dry gas meter; however, in Aluar each cassette arrangement is connected to its own dry gas meter, which allows the F^- concentration to be

determined for every cassette arrangement. Potroom concentrations are then calculated taking the average of all 4 concentrations.

Sampling Period

Local authorities require us to conduct a minimum of 3 runs per potroom per month with duration of at least 24 hours or one complete cycle of the four main operative phases executed on a pot: anode change, metal tapping, anode covering and process controls. Having to manage our available resources as well as potroom accessibility, different sampling periods have been implemented since the beginning of sampling, with 24, 32, 40 and 48 hour durations.

Cassette Location

Cassette arrangements combined with anemometers and temperature sensing devices enable us to determine the mass flow rate of pollutants, are located across the potroom roof, evenly spaced holding at least 8% of the total length. See figure 2.

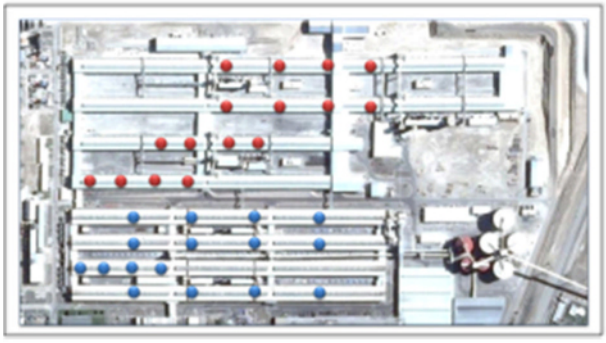

Figure 2 –Cassette Arrangements

The same procedure is not performed in all pots at the same time, but different tasks are distributed in groups of pots ("operative phases"), thereby permitting our resources to be optimized. Figure3 shows how the procedures are programmed for a particular shift.

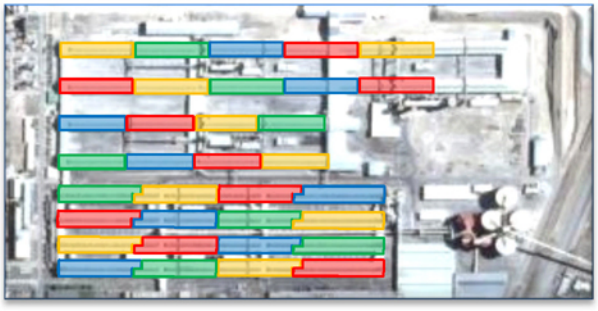

Figure 3 – Pot Operations Scheme

The references for the figures is green for anode change, yellow for process control, red for metal tapping and blue for anode covering.
This being the case, the scheme of procedure during the next 8 hour shift, would be like the one shown in Figure 4.

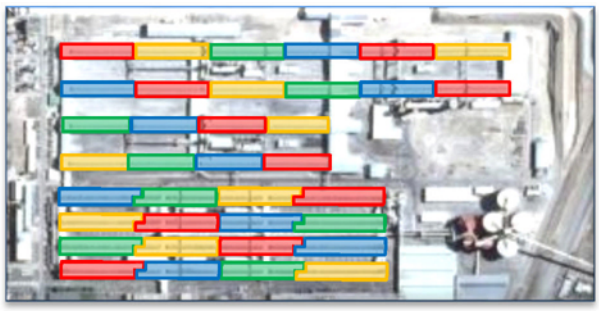

Figure 4– Pot Operations Scheme for next shift

Because of a very tight schedule, it is not always possible to perform a run of a 32 hour period. The next exercise presents the hypothesis that sampling period has little effect on Ft calculation. In case the proposition is confirmed, this would allow adapting the sampling to the available resources.

Proposal 1

Although the complete cycle of the pot lasts 32 hours (four tasks, each one performed in an 8 hour shift), during 24 hours the four cassettes in a single potroom have passed through all the stages of the cycle with no negative effect on the estimation of Ft concentration.

Analysis 1

The null hypothesis of no sampling period influence in the F^- concentration was investigated for the Aluar type PFPB potlines (potlines A and B). The same analysis was then conducted for the AP type PFPB potlines (Potlines C and D). The data collected was assembled according to sampling time of 24, 32, 40 and 48 hours. This is presented in Tables 1 and 2.

	Aluar Technology Potlines Ft Concentration (mg/Nm^3)			
Sample Time (hours)	24	32	40	48
Median	0,52	0,52	0,49	0,55
95th Percentile	0,80	0,80	0,92	0,96
5th Percentile	0,39	0,28	0,37	0,36
N	822			

Table 1 –Aluar Technology Data

	Pechiney Technology Potlines Ft Concentration (mg/Nm^3)			
Sample Time (hours)	24	32	40	48
Median	0,45	0,43	0,45	0,48
95th Percentile	0,58	0,54	0,63	0,61
5th Percentile	0,37	0,37	0,34	0,35
N	829			

Table 2 – Pechiney Technology Data

For our statistical calculations we selected the SPSS software. No significant differences were found in each case. See Table 3 for Aluar technology and Table 4 for Pechiney technology.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Conc Ft Aluar is the same across categories of Sample Time.	Independent-Samples Kruskal-Wallis Test	,237	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 3–SPSS calculation for Aluar potlines

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of Conc Ft Pechiney is the same across categories of Sample Time.	Independent-Samples Kruskal-Wallis Test	,554	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 4–SPSS calculation for Pechiney potlines

Measurements have to be done with a limited amount of resources. The goal of this analytical exercise is to use statistical modeling to find the optimum case where we have a good balance between the number of resources involved, the number of measurement conducted and a reliable outcome of emission data that represents the operation.

Proposal 2

In order to reduce the amount of monthly samplings, several statistical comparisons were made between data collected during 19 months of sampling and the hypothetical results obtained as if only part of the sampling was performed instead and how this would impact in long term fluoride emission.

The reduction of measurements would not affect the process control, since sampling and results obtained are mainly used for reporting to Environmental Authorities.

Alternative 1

Ft concentration of a potline estimated from three monthly runs in each of the 2 potrooms of the potline (e.g. potroom #1 and #2 for potline A) vs Ft concentration estimated from three monthly runs performed in only one of the potrooms of the potline, alternating potlines on a monthly basis

Alternative 2

Ft concentration of Aluar cell technology estimated from the average of three monthly runs in each potroom of Aluar reduction cells (potroom#1 to #4) vs Ft concentration estimated from three monthly runs performed in only one of them. The potroom to be measured would vary from month to month.
The same exercise is carry out for AP18 cells, comparing the Ft concentration estimated from the average of three monthly runs in each potroom (#5 to #8) vs Ft concentration estimated from three monthly runs performed in only one of them.

Alternative 3

Ft concentration of PFPB type potlines (Aluar and Pechiney) estimated from three monthly runs in each of the 4 potrooms of each kind, vs Ft concentration estimated from three monthly runs, each run executed in a potroom randomly chosen from the four (it could also be possible to execute 3 runs in the same potroom in one particular month).

Data collected is summarized in Tables 5 and 6.

	Ft Concentration (mg/Nm³)			
Potline	***A***	***A (Alternative1)***	***B***	***B (Alternative 1)***
Median	0,52	0,52	0,49	0,55
95th Percentile	0,80	0,80	0,92	0,96
5th Percentile	0,39	0,28	0,37	0,36
N	19			
Potline	***C***	***C (Alternative 1)***	***D***	***D (Alternative 1)***
Median	0,45	0,43	0,45	0,48
95th Percentile	0,58	0,54	0,63	0,61
5th Percentile	0,37	0,37	0,34	0,35
N	19			

Table 5–Data for Alternative 1 Estimations

	Ft Concentration (mg/Nm³)		
Technology	***Aluar***	***Alternative - 2***	***Alternative - 3***
Median	0,55	0,55	0,52
95th Percentile	0,78	0,93	0,84
5th Percentile	0,42	0,39	0,35
N	19		
Technology	***Pechiney***	***Alternative - 2***	***Alternative - 3***
Median	0,46	0,44	0,44
95th Percentile	0,59	0,55	0,68
5th Percentile	0,36	0,35	0,31
N	19		

Table 6–Data for Alternative 2 and 3 Estimations

Analysis 2

The null hypothesis of no difference between previous estimation of Ft concentration and the alternatives was examined for the 8 cases presented with data acquired from 19 months of sampling (from September 2014 to May 2014). Once again the SPSS software was used for all the statistical computation. No significant differences were found in each case.
Alternative 1 shows we potentially can reduce the number of samplings by a half, whereas in alternatives 2 and 3 the number of samplings is reduced ever further to 75%. Results are shown in Tables 7 through 14.

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Potline A and Conc Ft Potline A - Alternative 1 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,212	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 7–Alternative 1 for Potline A

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Potline B and Conc Ft Potline B - Alternative 1 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,560	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 8–Alternative 1 for Potline B

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Potline C and Conc Ft Potline C - Alternative 1 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,153	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 9–Alternative 1 for Potline C

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Potline D and Conc Ft Potline D - Alternative 1 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,246	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 10–Alternative 1 for Potline D

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Aluar and Conc Ft Aluar - Alternative 2 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,896	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 11–Alternative 2 for Aluar Potlines

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Pechiney and Conc Ft Pechiney - Alternative 2 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,643	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 12–Alternative 2 for Pechiney Potlines

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Aluar and Conc Ft Aluar - Alternative 3 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,546	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 13–Alternative 3 for Aluar Potlines

Hypothesis Test Summary

	Null Hypothesis	Test	Sig.	Decision
1	The median of differences between Conc Ft Pechiney and Conc Ft Pechiney - Alternative 3 equals 0.	Related-Samples Wilcoxon Signed Rank Test	,777	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is ,05.

Table 14–Alternative 4 for Pechiney Potlines

Conclusion

No statistically difference was found between Ft concentrations obtained from different sampling intervals for the hypothesis raised in the first proposal.

The sampling little influence on results is expected to be a consequence of concentration being calculated for each cassette arrangement, rather than computing all the samples as one, besides all the cassettes are located above cell with different practices being executed.

All the alternatives presented in the second proposal showed no significant difference from the normal procedure in Ft concentration measurement. Number of potroom Ft concentration samplings per month can be reduced by at least 50% with no serious deterioration of the accuracy and deviation in the long term Ft emission estimation.

References

[1] P. Navarro, C. Daviou, L. Daurade, "ALUAR'S al20 PROJECT: A SUCCESSFUL WAY UP TO 200kA", iv International Aluminum Congress (May 18th, 19th and 20th 2010 – Sao Paulo), p. 594-609.

[2] Method 14A – Determination of Total Fluoride Emissions from Selected Sources at Primary Aluminum Production Facilities – http://www.epa.gov/ttn/emc/promgate.html

[3] IBM - SPSS statistic_V20 (http://www-01.ibm.com/software/analytics/spss/)