

DEVELOPING A NEW PROCESS INDICATOR BASED ON THE RELATIONSHIP BETWEEN AN ELECTROLYSIS CELL IMPURITY BALANCE AND ITS INCIDENTS

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Abstract

Aluminerie Alouette recently studied the relationship between electrolysis cell operation and their impurities' balance. It was observed in some cases that the concentration of impurities in the metal is lower than expected from raw material mass balance, mainly for iron, gallium, titanium and vanadium. These cells were inspected to find the cause of the imbalance; methodology and results of the inspection are presented in this paper. Analyses regarding cell performance were conducted with regard to cell impurities distribution (metal/crust/gas duct). The factors correlating these phenomena are discussed, with focus on operational results. It was found that anodic incidents are strongly related to very low impurity concentrations in the aluminium and it was possible to develop an indicator at Aluminerie Alouette to quickly detect anodic incidents using vanadium content in the aluminium. This process tool is presented and discussed in the article.

Preface

Aluminerie Alouette, as a leader in low ACD operation has to develop new ways to think and new methods to face difficulties in an uncharted window of operations.

With a technology pushed to its limit, every indicator that gives Alouette an early sign of malfunctions of their electrolysis cells may make the difference in terms of employees' workload or in production.

This paper presents one indicator developed by employees of Aluminerie Alouette using different tools: data mining, lean six sigma, etc.

Vanadium level as well as the level of standard deviation of vanadium have been used successfully for the last two years for detection of anodic incidents and is now a part of daily routine.

Introduction

To achieve efficient results, process engineers and technicians look at numerous key performances indicators (KPI) daily or weekly. Within those KPI, the iron and the silicon level in the molten aluminum are an important point of interest. Usually, the focus is primarily on the highly contaminated electrolysis cells. However, on some occasions, it was observed that the iron level in the aluminum was lower than expected from the material balance of these electrolysis cells. The iron concentration could reach half the calculated value. Similar results were found for gallium, vanadium and titanium. It was mentioned in a paper from Zhang et al.[1] that the impurity

partition is dependent of the operating practices and condition. Therefore, Aluminerie Alouette decided to investigate some cells to find a common cause explaining the phenomenon observed. This paper presents the numerous steps and results from Alouette in this investigation.

Initial case

Iron mass balance

There are many possible ways used to follow the impurity distribution in aluminum electrolysis pot rooms, like the average concentration, standard deviation, over limit cells, etc. On the other hand, the simple method introduced by Stephen Lindsay[2-4], which is called visual mass balance illustrates perfectly the scenario at Aluminerie Alouette. Using a cumulative distribution, it is possible to count and identify the different cells within the distinct groups of electrolysis cells.

- Under balance : under the normal material balance of the cell
- In balance : iron level close to normal material balance of the cell with moderately oxidized anodes (500 to 750ppm)
- Contaminated : iron level above the expected values of iron caused by small exposure to the anode stub (750 ppm to 1000 ppm)
- Highly contaminated: very high iron level caused by major contamination (important exposure of the anodes, cathode bar exposure, etc.) (1000 ppm and higher)

The following visual mass balance illustrates the Fe contamination level from Aluminerie Alouette electrolysis cells during the first investigation.

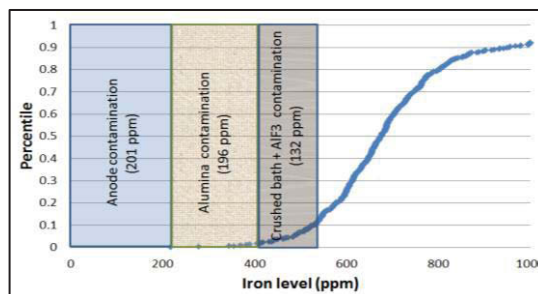


Figure 1: Visual mass balance for Fe contamination of the electrolysis cells (highly contaminated cells excluded)

On Figure 1, our interest is for the “under balance” cells. From our calculated value, 10 % of cells are under the expected

material balance regarding their iron contamination. Three reasons can partly explain why the cells were under balance.

1. Under production of bath :
If the production of cryolite is lower than usual, it is plausible that the crust dissolution was lower as well. Therefore, the iron input coming from the crushed bath is negligible, leading to a value lower than expected from the overall calculation.
2. Segregation of the alumina in the HPDS system :
The distance from the gas treatment centers to the end of lines is hundreds of meters. It is plausible that the fine fraction of the alumina (higher Fe content)[5] is dosed to the closer cells and not to the extremities of the system.
3. Iron release in the cell duct is significant : According to some studies[1, 6], there is a fraction of the iron that does not go to the aluminium. This fraction depends on the cell operating conditions and in many cases, this fraction might be significant.

To examine these hypotheses, the fifteen pots with the lowest iron were selected and studied regarding the bath production and their distance from the start of the HDPS. It was found that some of the cells were not producing electrolysis bath as they should. However, 62.5% of those cells were found with an iron content value lower than the 400 ppm limit that would be expected if no iron contamination at all would come from the crushed bath. Therefore, bath production cannot explain all by itself the observed results.

If we look at the distance factor, the selected cells are evenly divided across the potrooms indicating that this factor alone does not explain the results.

Then, if we suppose that these two hypotheses might be simultaneously happening in some cells, the iron input from both the alumina and the crushed bath would be reduced or eliminated. In “extreme” conditions, this could lead to an iron content of 202 ppm. Assuming that every cell considered are in those “extreme” conditions, with regard to their distance and bath production, the material balance of only 60% of the selected cells could be explained. Therefore, it is evident that the third hypothesis (iron output in the cell duct) needs to be considered to explain why the remaining cells are still under the calculated material balance.

Balance of other elements

During the same period, the concentration in the aluminium of many elements has been investigated with hope of finding similar results. Hence, a cumulative distribution was performed for most of the elements that can be analyzed by Aluminerie Alouette’s laboratory. For some elements (Si, Na, P), no similarity with the previous results was found. However, when performing the analysis of the cumulative distribution for the gallium, titanium and vanadium, the findings were interesting.

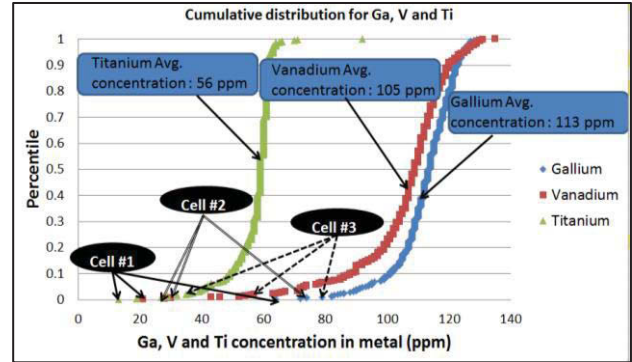


Figure 2 : Cumulative distribution for Ga, V and Ti. (Cell #1, #2 and #3 were the three lowest iron concentration on Figure 1)

We can see that the cells at the bottom of the curve for the iron contamination are the same ones that are in the lowest percentile of the curve for gallium, vanadium and titanium. The concentrations observed for these cells are lower than the expected material balance values and lower than the typical concentration in an electrolysis cell.

By examining the certificate of analysis for the primary sources of alumina and coke, we can see a significant amount of gallium coming from the alumina. On the other hand, vanadium is found mostly in the coke. Knowing that two unrelated inputs are affected, it is evident that the common cause of these low concentrations is related to the outputs of the cells. This favors the third mechanism described previously to explain the under balance cells.

Impurity partition factors

From the first analysis, it was shown that some elements must exit the electrolysis cell as dust through the cell duct. Many authors tried to explain these mechanisms and many hypotheses were made to explain the exact origin of the output. Goods [6] cited many of these authors in his thesis. It was proposed by many of them that titanium, lead, silicium and iron may exit the cell as volatile species (TiF₄, PbF₂, SiF₄ and FeF₄). It was also indicated that iron could react with carbon monoxide to create Fe(CO)₅ in some ideal conditions. Thonstad and al.[7] concluded that the transfer of iron, vanadium, nickel and copper are not accounted for by considering only evaporation and entrainment of solid particles must be considered as well. Frankenfeldt and Mannweiler [8] described how primary materials can be captured by the air flow from the cell and Azbel and al.[9] described how the electrolytic bath can form droplets during the normal process. For both these cases, the impurities inherently present in the primary material can be transferred to the duct and up to the gas treatment center.

Independent of the mechanisms, our interest is concentrated on the fraction of the impurities leaving the cells with the airflow (dust, droplet, or evaporated compounds) in comparison to the input. Bohm et al. [10] and Sparwald [11] introduced the distribution factors as :

$$\alpha = \frac{\text{impurities in pot gas}}{\text{impurities in original materials}}$$

From the distribution factor, and assuming that outputs from the bath are negligible, we can assume the following relation as well:

$$1 - \alpha \approx \frac{\text{impurities in metal}}{\text{impurities in original materials}}$$

Many authors [1, 6, 10, 12, 13] used these concepts and applied it in their study and respective technology when establishing a material balance. However, in 2013, Metson and al.[14] listed the most interesting studies in a table, with their respective technologies.

Table I: Table illustrating the partition factor (1- α) for various elements. [14]

	Tech1 [3]	Tech2 [4]	Tech3 [5]	Tech4 [6]	Tech5 [6]	Tech6 [2]
			Ardel	High purity trial	Avg. 12 references	NZAS
	Erfwerk		HAL-150			P69
	SW/BB		PF			CW/BB
	CPA		Pre-Bake			Pre-Bake
	125kA	140kA	150kA			150kA
	(1973)	(1976)	(1978)	(1988)	(1988)	(1996)
Ti	0.379	0.430			0.500	0.763
Fe	0.544	0.580	0.700	0.595	0.870	0.814
Ga	0.496		0.750	0.658	0.660	0.761
Si	0.918	0.930		0.952	0.950	0.980
P	0.143				0.090	
V	0.345	0.150	0.800	0.167	0.390	0.493
Ni		0.600	0.090	0.103	0.330	
Zn	0.800				0.660	
Cu			0.180		0.550	
Pb			0.320		0.560	
Mn					0.920	
Cr					1.000	
SW – Side Worked			PF – Point feed			
BB – Bar Breaker			CW – Centre worked			
CPA – Continuous pre-bake anode						

For the elements of interest (Ti, Fe, Ga, V), we can note that every one of them have important variation. This leads to two fundamental questions related to our approach:

1. Is the partition factor dependent only of the technology? (cell design, intensity, primary materials, etc.)
2. Can the partition factor be different for a single cell on a day-to-day basis?

As the technology is given at Aluminerie Alouette, it was not possible to conduct meaningful experimentation to find an answer to our first question. However, it was possible to analyze operational results from the cells on a daily basis.

Chemical analysis of the duct emissions is not included in the weekly routine of the cell operations. However, the chemical analysis of the aluminum is done almost daily for each pot. It has been determined that if the impurities correlation (1- α) is

used for the vanadium, the results should be significant within the set of the following facts and assumptions:

Facts

1. The main vanadium input in an electrolysis cell comes from the anodes. This input is constant based on the rate of carbon consumption
2. The vanadium input from the alumina is insignificant ($\approx 3\%-7\%$) in comparison to the feeding from the anodes
3. The vanadium level of the anodes only has small variations through time and depends on the primary sources of coke.
4. The variations in the anode compositions will take a complete anode cycle to be completely effective in the electrolysis cell.

Assumptions

5. Based on the results from Wrigge and Albers [15], under electrolysis conditions the vanadium concentration in the metal is almost unrelated to the concentration in the bath. Therefore, it is independent of the bath inventory of the cell.
6. The output of metal is constant and measured. Therefore, we assume that the metal inventory in the cell is approximately the same for the period analyzed
7. The loss of electrolytic bath is negligible. The main outputs of our cells (for the vanadium) are therefore the metal and the duct gas.
8. The expected concentration of vanadium at equilibrium in the electrolytic cell is similar to the average level of vanadium in the potline (105 ppm)

In agreement with those premises, the vanadium concentration in the metal for three cells was followed during a six-month period to see if the level of vanadium had important variations through time. Any significant variation in the vanadium concentration would indicate that the partition factor has changed during the cell operation.

Results shown in Figure 3,4 and 5 illustrate that a single cell can diverge from its normal state for a specific period of time.

A correlation analysis was performed using Statistica[16] to discover if any operation parameters were in correlation with the vanadium concentration. The following parameters were studied:

- Bath height
- Metal height
- Current intensity
- Bath tapped
- Metal tapped
- Number of alumina doses
- Number of AlF3 doses
- Cell's resistance
- Cathode resistivity
- Anode effect overvoltage
- Cell voltage
- AlF3 content in bath
- CaF2 content in bath
- Alumina's point feeders actions
- Time spent in high instability
- Time spent in low instability
- Number of alumina doses
- Age of the cell
- Bath temperature
- Iron content in the aluminium
- Silicon content in the aluminium
- Cell instability

In most cases, the correlation coefficient was lower than 0.4, indicating that the parameter correlates only slightly or not at all with the vanadium concentration. However, two possible

relations need more investigation due to a higher correlation coefficient. These investigations are not presented in the present paper.

Current intensity: It has been observed that a higher current intensity in the cells correlates with a lower concentration of vanadium in the aluminum.

Cathode resistivity: The correlation coefficient indicates that a higher cathode resistivity in the cells correlates with a higher vanadium concentration in the aluminum.

To evaluate the impact of anode effects and anodic incidents¹, both these discrete events were illustrated on the same figures as the vanadium content in the aluminium over time:

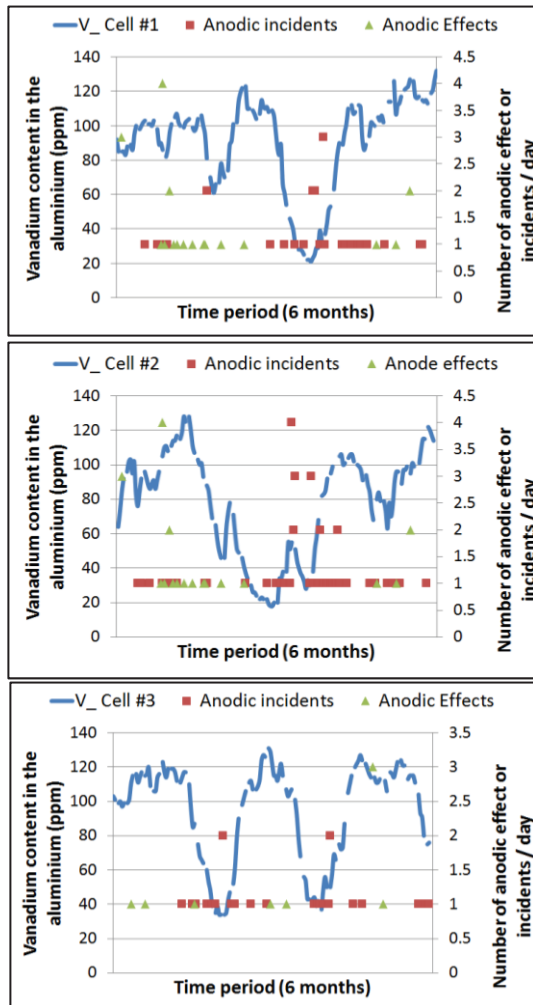


Figure 3, 4 and 5 : Variation of vanadium in time over a 6-month period for three cells. Discrete events (Anodic incidents and anodic effects) are included on the figures.

¹ The anodic incidents are considered to be similar to spikes (causing a local increase in the current intensity and an increase in temperature as well)

There is no correlation with the anode effects and the drop observed in the vanadium level. On the other hand, for every significant lowering of the vanadium concentration, a cluster of anodic incidents was observed in the aluminium reduction cells for the same period or very shortly after the lowest peak in the vanadium concentration. This is the most relevant correlation found for all the parameters analyzed.

As the facts and assumptions stated previously are correct or highly plausible, it follows that the partition factors for the vanadium can change through a short period of time. All of these variations correlate well with the anodic incidents observed in the same electrolysis cells. If the correlation is significant and repetitive, the daily analysis of the concentration of impurities in the aluminum could become an easy way to detect anodic incidents.

Correlation between anodic incidents and the vanadium content in the aluminium

To verify the correlation between anodic incidents and the vanadium content in the aluminium, it is postulated that the partition factor will change over time and these variations will be consequent with anodic incidents in the cell.

It is supposed that the anodic incidents will create local conditions that favor the evaporation of the vanadium (high temperature, high local current density, variation in the bath/metal flow, etc.) Henceforth, the concentration of vanadium in the duct system should rise.

Slaughaupt and al. [17] demonstrated that the crust over the anodes act as an in-situ scrubber. Therefore, it is plausible to think that a rise of the impurity concentration in the crust should be observed in the presence of anodic incidents, if our postulate is correct.

Finally, if most of the vanadium exits the cell through the duct, the vanadium in the aluminium should be diluted as more aluminium is produced each day and a fraction of its mass (aluminium and vanadium) is removed through the tapping operation.

Vanadium concentration in duct gas

During the studied period, a specific cell having all the necessary criteria was selected:

- Very low vanadium level in the aluminium
- Presence of an anodic incident
- Constant input variables through time

A sample of its duct gas was taken and analyzed for the elemental composition. At the same time, another sample was taken on the adjacent cell (with no anodic incidents and no vanadium variations). Results from the analysis are presented in Table II

Table II : Elemental analysis of the duct gas

	Cell #1 (with anodic incident)	Cell #2 (without anodic incident)	Cell #1 / Cell #2 ratio
Fe content (mg/m ³)	0.70	0.041	17.1
Pb content (mg/m ³)	0.38	0.10	3.8
V content (mg/m ³)	0.14	0.010	14
Ni content (mg/m ³)	0.19	0.013	14.6

The results show clearly that the concentration level in the gas for vanadium, nickel and iron is more than ten times higher in the cell with an anodic incident than in the one without. This is in agreement with our main assumption.

Moreover, it is well known that the impurities exiting the cells as dust are caught in the gas treatment center and re-introduced in the electrolysis cells. Therefore, the impurities exiting through the duct can be considered as outputs for a single cell but this is not an output for the electrolysis pot rooms as a whole.

The vanadium concentration in the aluminum among all the potrooms was followed during an anodic incident crisis and an interesting phenomenon was observed.

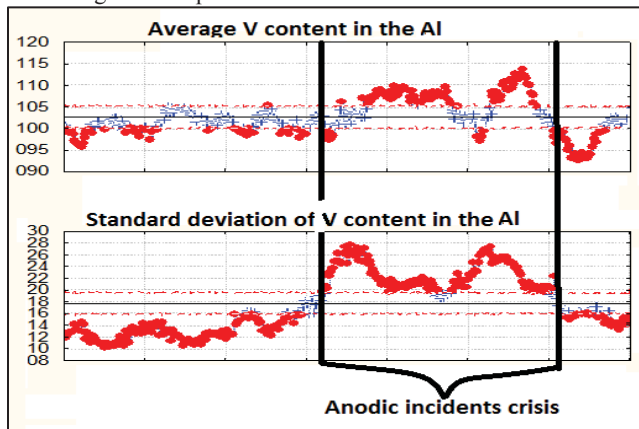


Figure 6 : Average and standard variation of the vanadium content in the aluminum for every cell in the potrooms during an anodic incident crisis.

As we can see on Figure 6, during the studied period, the average value of the vanadium in the potrooms did not change significantly for the selected period ($\pm 10\%$). The variations are accounted for by the coke contamination variations observed for the production of the anodes in the same period. However, a significant increase in the standard deviation (more than 100%) can be observed during the anodic incidents.

This is again in agreement with our postulate. If the vanadium from problematic cells goes out through the gas duct, these cells are lowering their vanadium content in the aluminum. However, the vanadium is redistributed equally across every electrolysis cells, which feeds a richer concentration of vanadium to the non-problematic cells; therefore, these cells raise their concentration of vanadium in the aluminum explaining the raise of the standard variation.

Impurity concentration in the crust

To study a more representative group, a process technician identified ten cells with anodic incidents across the pot rooms. Then, a sample of bath crust was taken directly from the top of the problematic anode to analyze the impurity content. For the same period, eight very stable cells with regard to anodic incidents were selected as a standard group.

At the time of this paper, only the analysis for the iron content had been performed. However, as the results from Figure 2 suggest, it is very likely that a similar behavior would be observed regarding the vanadium concentration. The samples

were measured using the ICP-OES standard procedure. Results from those measurements are presented below:

	Average iron concentration (ppm)	Standard deviation (ppm)
With anodic incidents	2804	2306
Without anodic incidents	1539	253

From these results, it is clear that the average concentration of impurity in the crust is higher when an anodic incident occurs. The standard deviation indicates that the concentration of iron can rise extremely high in some cases. One sample of crust was measured with a concentration of iron higher than 8000 ppm.

Assuming that the vanadium concentrations behave similarly, these results confirm our main assumption.

Vanadium dilution in the metal

For a better understanding of the vanadium evolution, the concentration of vanadium in the aluminium over time was studied using a daily evolution graph (figure 7). Four sets of data were collected from figures 3, 4 and 5 to illustrate the behavior of the vanadium concentration in the aluminium as it is dropping. The concentration was normalized by the original concentration in the cell prior to the drop. The additional curve represents the ideal dilution that would occur if no inputs of vanadium were added to the cell during the selected period.

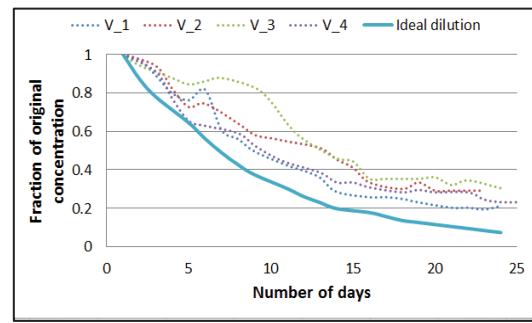


Figure 7 : Dilution of the vanadium in the aluminium

From its starting point on day one, the average concentration drops for fifteen days with a slope very similar to the ideal dilution. However, contrarily to a dilution where there is no input, the curves do not tend towards zero. As a matter of fact, the vanadium concentration leans towards a vanadium concentration of 20-40 ppm illustrating that some vanadium still enters the aluminium as input. In those conditions, we can confirm that only 20 to 40% of the vanadium reaches the aluminium while the remaining vanadium input must exit through the gas duct or the crust.

Indicator developed by Alouette to identify cells with anodic incidents

As a result of this study, Alumerie Alouette developed an indicator to detect the presence of electrolysis cells with a low vanadium concentration in the aluminium. This indicator does not require added sampling, nor any extra analysis above what is already done in the weekly routine.

Based on the vanadium level from the raw materials, a process technician defines a lower limit in the vanadium

concentration to identify an under balance cell. This limit is generally set to 70 ppm. Then, the indicator lists every electrolysis cells below the fixed limit. The results listed show the last measured level of vanadium as well as the value and variation from the three prior measurements. Therefore, the process technician has enough information to see if the variations are representative of the dilution curve illustrated in Figure 7. If the interpretations of the technician lead to a positive result, he will go and investigate the cell on site to find the source of the anomaly.

Success rate

When using this indicator, there is a need to investigate the electrolysis cell on site. Hence, this tool must be efficient and the total number of false diagnostics must be minimal. The efficiency of this tool is based on the total number of cases detected and the number of false diagnostics.

$$Efficiency = 1 - \left(\frac{Number\ of\ false\ diagnostics}{Total\ number\ of\ cells\ investigated} \right)$$

For five days, every case reported by the indicator have been investigated with attention to anodic incident that raises the anode current intensity over the standard limit of operation. A total number of 77 cells have been examined. The anode voltage was measured for every anode in those cells and only six cells resulted in a false diagnostic. Therefore, the indicator efficiency is approximately 92% showing that the indicator can be used efficiently in the smelter with almost no negative impact on the daily routine of operation.

Conclusion

Based on the material balances of an electrolysis cells, it was found that some cells are lower than expected when looking at the concentration of impurities in the aluminium. Fe, Ga, V and Ti are the elements most likely to be lower than the expected concentration because of their possible outputs through the gas duct.

By following the vanadium concentration, it was shown that the partition factor of these elements might undergo significant variations caused by the operating conditions of the cells. A correlation between a low concentration of vanadium in the aluminium, an higher output through the gas duct and the presence of anodic incidents in the cells was hypothesized and confirmed.

Based on these results, an efficient indicator was developed at Aluminerie Alouette to easily detect cells with anodic incidents.

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