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EFFECT OF OPERATIONAL PARAMETERS ON THE BEHAVIOR OF PHOSPHORUS AND SULFUR IN ALUMINUM REDUCTION

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Abstract

Impurities in the electrolyte of an aluminum reduction cell are known to affect current efficiency and other aspects of potroom operation. Traces of phosphorus and sulfur are generally present in the cells and their behavior is of interest due to their known adverse effect on the process of aluminum production In this study, data analysis was performed on the phosphorus concentration and different process parameters registered during the three years of daily measurements at the Alcoa Fjarðaál smelter. Experimental samples taken during power outages were also collected and analyzed for the sulfur and phosphorus concentrations in the bath.

High bath height was found to be correlated with higher phosphorus concentration in the metal. Moreover, there is a very strong negative correlation between superheat and phosphorus in the metal. Elemental analysis shows an increase of the phosphorus and sulfur concentration during power outages.

Introduction

Most of the phosphorus in an industrial aluminum reduction cell originates from alumina and aluminum fluoride additions. Phosphorus can escape mostly with cell gases, but also with tapped aluminum [1, 2]. Typical levels of P_2O_5 reported by Thonstad et al. in primary alumina is $4 - 11$ ppm [1]. Although this concentration may seem small, phosphorous is resistant to leave the cell, and combined with the rate of alumina feeding and use of dry scrubbers a build-up of phosphorus may occur in the bath. Primary alumina, which is being used as scrubbing agent to clean the emitted gases from the cell, becomes enriched with phosphorus in a closed loop system. Danek et al. [3] has performed a mass balance for the phosphorus distribution, where primary alumina contained phosphorus of 3.8 ppm, the secondary alumina from the dry scrubber 33 ppm, the bath 39 ppm and the metal 3.5 ppm. The enrichment of phosphorus debases metal purity and current efficiency. According to literature, current efficiency decreases by about 1% for each 100 ppm of phosphorus in the bath [1, 2]. In a previous work the present authors found that phosphorus can decrease current efficiency in a laboratory cell even up to 2.4 % at high current density (1.5 A/cm^2) and low concentrations up to 220 ppm in the bath [4].

Sulfur is naturally found in fossil carbon-based materials and will therefore be present in anodes used for aluminum production. The option of sulfur removal from aluminum cell flue gas for environmental reasons opens up the possibility to use anodes with a higher sulfur content made of more affordable raw materials. As the anode is in direct contact with the bath, it is only interesting to investigate which effects increased exposure of the bath to sulfur from the anodes will have on the operating conditions in the cell. In this study the following tasks were done to achieve better understanding of the impurities discussed above

- Statistical analysis of how phosphorus concentration correlates with different process parameters
- Experimental analysis of phosphorus and sulphur during current interruption

The aim of the data analysis was to find the reason for cell-to-cell variability in phosphorus levels. The phosphorus concentration was compared with different process parameters, such as temperature, superheat, bath height, cell age and noise.

Sampling for phosphorus analyses in the metal is done routinely for each cell, but not for the phosphorus concentration in the bath. However, Haugland et al. [5] introduced the rule of thumb where the relationship between the bath and metal concentrations of phosphorus is tenfold. We can therefore expect that when the phosphorus concentration increases in the metal, it is due to an increase of the phosphorus concentration in the bath.

Additionally, the behavior of phosphorus and sulfur during power outage was studied. Current interruption affects both the CO_2 and the magnetically driven convections. Convection in the cell slows down almost to a minimum when no current passes through the cell [6]. Only natural convection due to density differences will still occur. We would expect the concentration of dissolved aluminum in the bath to increase, and metallic impurities to undergo chemical reactions and sink to the bottom or rise to the surface of the bath, depending on their specific weight relative to that of the bath.

When the temperature decreases, the side ledge thickness and the concentration of excess AlF_3 in the bath increase [1]. Even though the side ledge is essentially pure cryolite, it may contain impurities. It has been reported by Thonstad et al. [1] that carbon serves as a nucleation substrate for impurities. Thisted [7] also studied the behavior of phosphorus during current interruption. She observed that the phosphorus concentration in the bath decreased, and explained this behavior as the result of the presence of carbon particles in the cell. She concluded that carbon can absorb impurities such as phosphorus and when the CO_2 driven convection ceases, these impurities attached to carbon particles are transported to the surface. This occurs because the surface interfacial tension between carbon particles and the bath is high.

Implemented Methods for data analysis

Regression analysis was run between the phosphorus concentration in the metal and the different process parameters. According to this regression analysis p-values were estimated and the extreme low values were selected. The parameters, which showed pronounced correlation, will be discussed in this paper. Further, to construct trend plots, the phosphorus concentration in the metal was divided into several categories: up to 4 ppm, 4-9 ppm, 9-14 ppm and 14-20 ppm. In industry, a phosphorus concentration of up to 4 ppm is considered to be low and a concentration greater than 9 ppm is considered high. Error bars represent standard error of the mean, which is calculated using:

$$Standard\ error\ of\ the\ mean = \frac{\sigma}{\sqrt{N}}$$

where σ is the population standard deviation and N is the sample size.

Experimental Set-up

Measurements were performed on one cell with prebaked anodes. The procedure for selecting a cell was as follows: data from the last three months was reviewed to find a cell which had naturally high phosphorus concentration in the metal and had representative parameters, such as temperature, age, bath ratio, base resistance, and noise for the whole population.

Bath and metal samples were collected before, during and after the current was cut, and analyzed as a function of time. Bath samples were collected from the surface, in the middle and close to the metal (end bath). The sampling device for taking bath samples was adopted from Rolseth [8]. Figure 1 shows a photograph of the sampling device. The position of the cup can be regulated with the height adjuster, which allows taking bath samples at different heights of the bath. The bath sample weight is up to 40 grams.

Figure 1. Sampling device used for taking samples during power outage

While the current was at a steady state during normal operation, sampling was carried out at a regular hourly interval. During the controlled power cut, sampling was carried out at regular intervals of about 15-20 minutes. In the controlled power cut, the current was ramped slowly down and then cut to zero, and after one and a half hour ramped up again slowly step-by-step until full power was achieved.

The metal samples were collected with a steel ladle. The phosphorus and sulfur concentrations in the bath samples were found by analysis of X-ray Fluorescence. The phosphorus concentration in the metal was analyzed by an Optic Emission Spectrograph.

Results and Discussions

Statistical analysis

Measurement data in the period from January 2011 to December 2013 were examined. As mentioned above the metal sampling is made routinely: every 36 hours or even more frequently, depending on the cell condition. Temperature, superheat and bath height are measured usually at the same time. In order to obtain sensible information and construct trends, data can be grouped either by averaging the process parameters or phosphorus concentration. For practical reasons, data was mostly averaged into phosphorus groups: up to 4 ppm, 4-9 ppm, 9-14 ppm and 14-20 ppm.

Figure 2 shows that the phosphorus concentration in the metal increases with increased bath height. A possible explanation for that can be related to the anode effects. It is known that low bath height gives higher anode effect frequency [9].
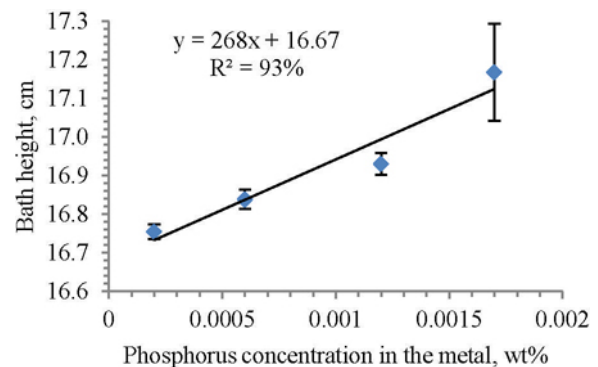

Figure 2 Bath height versus phosphorus concentration levels in the metal (January 2011-December 2014). The error bars were constructed using standard error of the mean.

During anode effect the bath gets strongly overheated, up to 50-100 degrees [1]. This could lead to evaporation of phosphorus species from the bath. In a modern smelter anode effects are killed immediately, and overheating of the bath should be limited. However, we can expect that the working surface of the anode will get hot. If anode effect is the reason for the reduction of the phosphorus concentration, then it may be due to anode effect cleaning the anode surface.

Due to strict regulations of emissions, experiments with phosphorus concentration and anode effect could not be conducted at the smelter. However, there were indications that the phosphorus content in the metal could decrease drastically during anode effect. The reason for this is not known. We have observed one incident where five repeated metal samples were collected before and after an anode effect in a cell with a high level of phosphorus. In other cases, the phosphorus concentration was too low to see any change. Five samples were taken before the anode effect (09:00) and five samples were taken after the anode effect (22:40) from the same cell. Anode effect took place around 21:00. In Table 1 the phosphorus concentration in the metal before and after the anode effect is listed. Information regarding the anode effect duration can be found in Table 2.

According to Table 1, the phosphorus concentration was reduced from 0.0012 wt% to 0.0009 wt% after the anode effect. The phosphorus concentration in the bath dropped from 0.0140 wt% to 0.006 wt%. As mentioned previously this is based only on one

case, more research has to be done to confirm the link between anode effect and phosphorus.

Table 1 Phosphorus concentration in collected metal samples before and after anode effect in cell no A016. In the first column, each number represents one sample.

Number of samples	P % Before AE	P % After AE
1	0.0011	0.0009
2	0.0011	0.0009
3	0.0013	0.0008
4	0.0014	0.0009
5	0.0013	0.0008
Average	0.0012	0.0009

Table 2 Information regarding anode effect strength and duration in the A016 cell.

Local Time	AE-Time above 8 volts, sec	AE-Time below 2 volts, sec.
7/22/2014 20:55	4	27
7/22/2014 21:00	32	68
7/22/2014 21:05	11	24
7/22/2014 21:10	0	1

Figure 3 shows a plot of bath temperature as a function of phosphorus levels in the metal. It follows a nonlinear behavior, where at high temperature (968°C) low levels of phosphorus are found, and the effect evens out at higher phosphorus levels. Haugland et al. [6] studied phosphorus concentration as a function of temperature from industrial data. She found that the phosphorus level in the bath and in the metal phase decreased with increasing cell temperature.
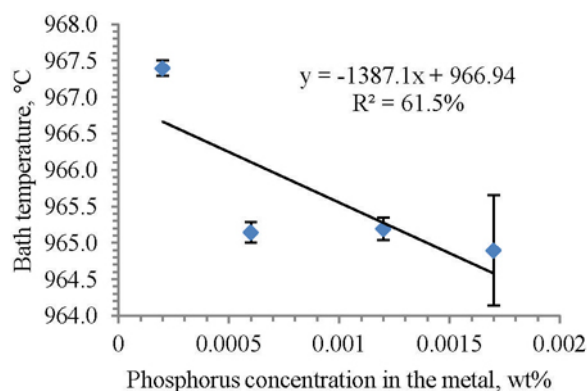

Figure 3 Bath Temperature versus phosphorus concentration levels in the metal (January 2011-December 2014). The error bars were constructed using standard error of the mean.

Another operational parameter we have looked at is superheat. Superheat is the difference between the bath temperature and the liquidus temperature; therefore, any change in superheat will result in change of thickness of the side ledge. At higher superheat the ledge is melted and the bath is diluted, additionally, the increased bath temperature facilitates the evaporation of phosphorus-containing species. A strong correlation between phosphorus levels in the metal and superheat temperature was found, see Figure 4.
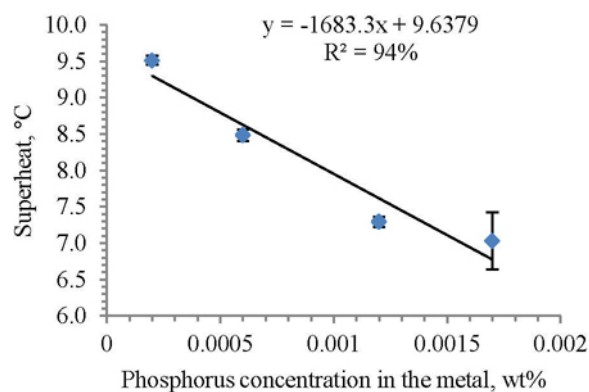

Figure 4 Superheat versus phosphorus concentration levels in the metal (January 2011-December 2013).

Figure 5 was constructed by averaging the daily data into years and creating 5 intervals: 0-1 year, 1-2 years, 2-3 years, 3-4 years, and 4-5 years after startup. This makes it easy for the reader to see the development of phosphorus over 5 years.

From the graph it can be concluded that phosphorus coming in with the raw materials continues to accumulate in the cell over the years. The graph shows 0.7 ppm increase of phosphorus in the metal per year. Danek et al. [4] concluded from statistical analysis that the content of P_2O_5 in the electrolyte decreases; this is not confirmed here. Therefore, it is important to check the raw material quality, since once phosphorous is in the system, it is hard to get rid of the phosphorus. Another option will be removal of impurities from the secondary alumina. Considerable work has been done on this subject [10, 11].

Apparently something was happening between year 2 and 3. Both values are shifted from the linear relationship, indicating that a change in raw material purity had occurred or alternatively that the operational strategy with regard to heat balance in the cell may have changed.
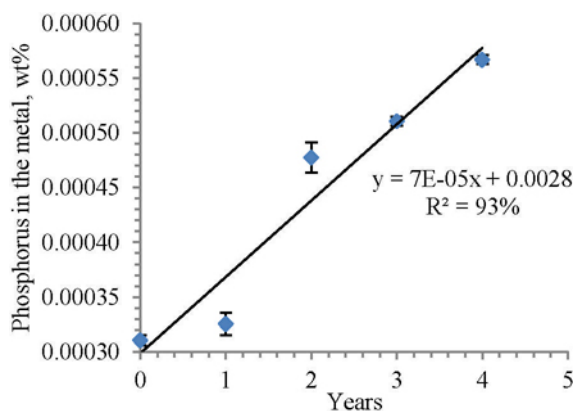

Figure 5 Evolution of the phosphorus concentration in the metal over 5 years after startup (January 2011-December 2013).

Experimental analysis

Results for the phosphorus concentration in the bath as a function of time by current interruption are plotted in Figure 6. The phosphorus concentration shows a slight increase during the

current interruption at all bath heights, followed by a decrease. After ramping up the current, the phosphorus concentration shows a steady decrease towards the previous concentration level.
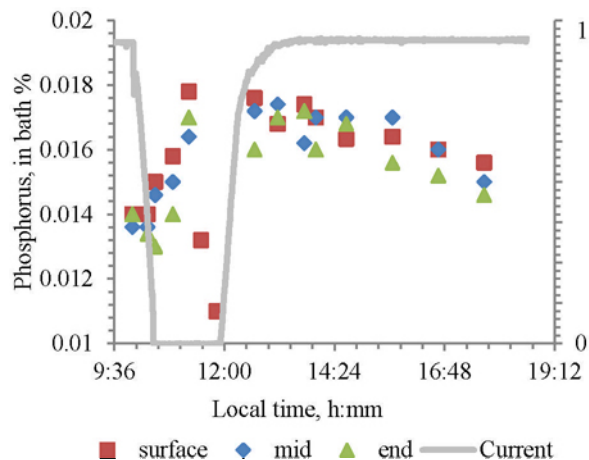

Figure 6 Concentration of phosphorus in the bath and line current as a function of time.

The sampling in the middle of bath and close to the metal pad was impossible after half time of the current interruption. The bath was mixed with aluminum which made it difficult to take samples at all bath heights. However, there was no problem in metal sampling.
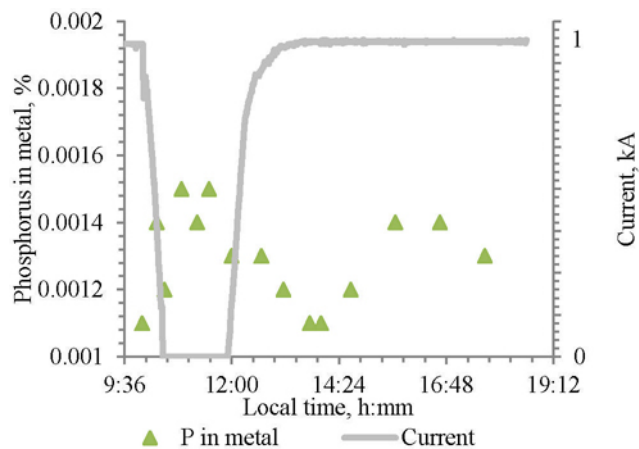

Figure 7 Concentration of phosphorus in the metal and the line current as a function of time.

Figure 7 shows the phosphorus concentration in the metal during and after the current interruption. The phosphorus concentration in the metal appears to rise during power outage, which supports the outcome in Figure 6.

Figure 8 shows the concentration of sulfur in the bath when the current had been interrupted. Increase of both impurities during power outage might be due to decreased convection, which, as a result, lowers the ability of the phosphorus and sulfur species to escape through the gas phase either as gaseous species or together with carbon dust particles. There is another hypothesis that phosphorus and sulfur might come from the anodes. When the current is cut, the cell acts as the battery and the anode is no longer positively charged, and it releases phosphorus anions which were accumulated during electrolysis back to the cell. As mentioned in the introduction, Thonstad and Thisted observed the attachment of phosphorus on carbon particles, thus this adherence during polarization might be an enhanced effect.
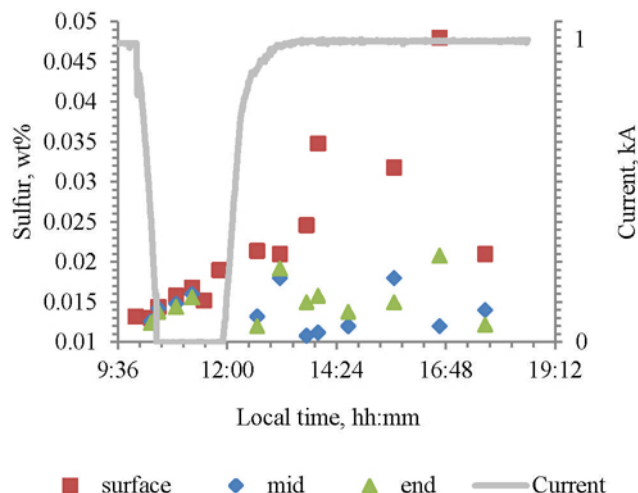

Figure 8 Concentration of sulfur in the bath and line current as a function of time.

The sulfur concentration in the bath, on the surface, and close to the metal have similar concentrations before and during the current interruption. Moreover, after the power is resumed, the data points appear scattered compared to those for phosphorus (see Figure 8). The detection limits for phosphorus and sulfur are 20 and 40 ppm, respectively. Since the detection limit for sulfur was higher and data points for sulfur might bear concern, it was decided to check the method of analysis. A predetermined amount of sodium sulfate was mixed with crushed bath from the cell and analyzed with XRF. Figure 9 shows that XRF is actually very accurate in determining the sulfur concentration.
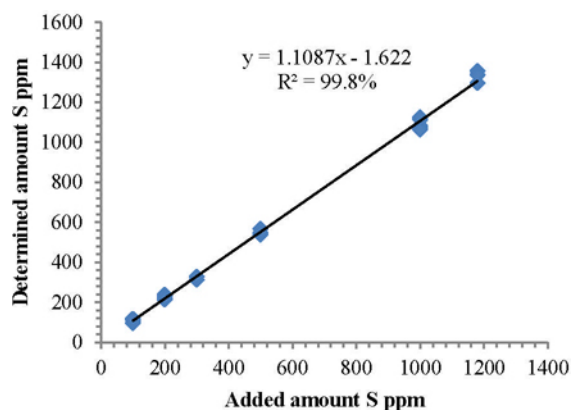

Figure 9 Comparison of added and analytically determined sulfur concentration

A possible explanation for the fluctuation in the data points after the power was resumed, is that some sulfur species are attached to carbon particles, and when the current is resumed, the gas evolution starts and therefore, the convection in the electrolyte will be strongly increased. The carbon particles will be mixed well, carrying sulfur along.

In one of the experiments during normal operation, bath samples were taken by an iron spatula, which was dipped into the bath and frozen bath was collected from it. The bath samples were analyzed by XRF and the carbon content in them was analyzed by LECO. Figure 10 shows the sulfur concentration in the bath as a function of the carbon concentration. It can be seen the sulfur concentration depends significantly on the concentration of carbon dust in the bath.

Scanning Electron Microscopy (SEM) analysis was performed on one piece of the bath sample taken by means of the iron spatula. The sample contained dark spots, which were carbon particles and white a white area which was the bath. The averages over several white and dark spots are shown in Figures 11 and 12 respectively. A comparison between them is illustrated in Table 3. As shown in Table 3, sulfur comes with carbon, therefore, the carbon dust will be contaminated with sulfur. Special care should be taken when sampling the bath in order to avoid misinterpretation of the sulfur concentration due to the presence of carbon dust. The amounts of O, F, Na, Al and Ca correspond to a normal bath composition with NaF/AlF3 molar ratio 2.6
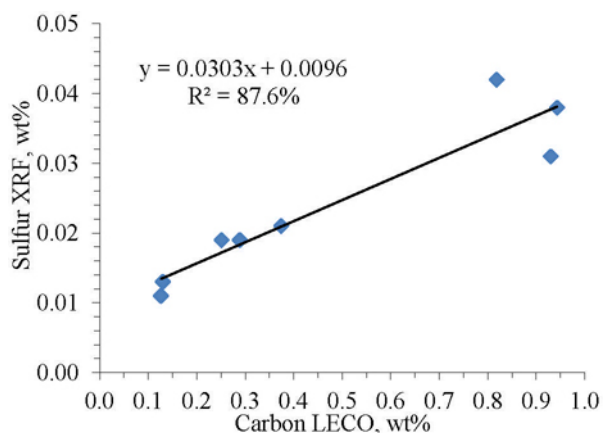

Figure 10 Sulfur concentration in the bath determined by XRF versus carbon concentration in the bath determined by LECO
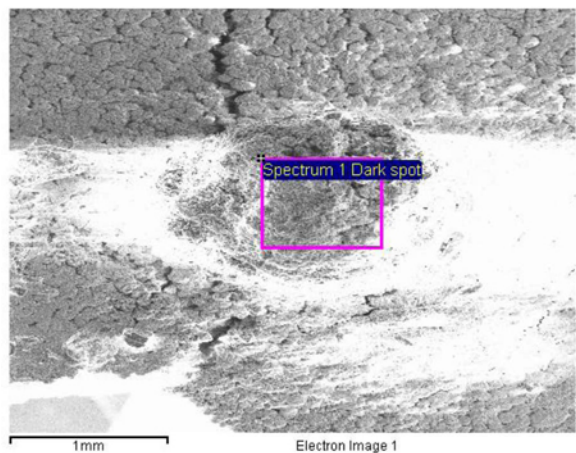

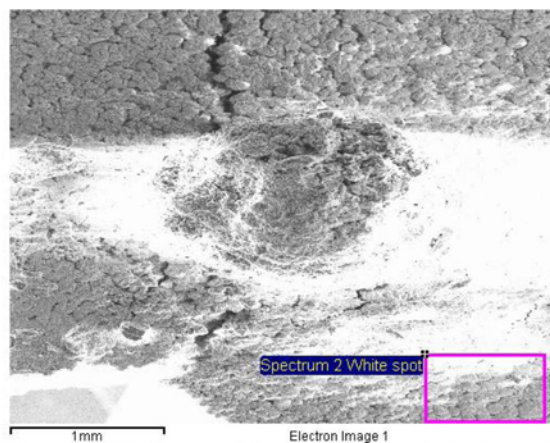Figure 11 SEM image of the dark spot on the bath sample

lFigure 12 SEM image of the white spot on the bath sample

Table 3 Comparison of the element concentrations between black spot area and white spot area of the bath sample.

Element	Weight%	Weight%
	Black spot	White spot
C	14.04	0.77
O	6.15	1.32
F	39.16	53.79
Na	21.19	29.66
Al	12.65	12.81
P	**0**	**0**
S	**1.41**	**0**
Ca	1.49	1.65
Fe	0.71	0
Ni	3.2	0
Totals	100	100

Conclusion

It can be concluded that the cell to cell variability of phosphorus depends on a number of operational process parameters. Lower superheat and higher bath height were found to be strongly correlated with higher phosphorus concentration. The phosphorus concentration in the metal is also shown to increase with cell age. This is attributed to that phosphorus introduced with raw materials stays in the electrolyte, accumulating over time. Chemical analysis shows that sulphur in the bath increases with the content of carbon dust. SEM analysis clearly indicates that sulphur is bound to carbon dust dispersed in the bath.

An increase of phosphorus and sulfur concentration in the bath was found during power outages.

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References

1. J. Thonstad, P. Fellner, G.M. Haarberg, J. Híveš, H. Kvande, and Å. Sterten *Aluminum electrolysis – Fundamentals of the Hall-Héroult process*, 3rd edition (Aluminum-Verlag GmbH, Düsseldorf, Germany, 2001), 227

2. K. Grjotheim and H.Kvande, *Introduction to Aluminum Electrolysis*, (Aluminum-Verlag GmbH, Düsseldorf, Germany, 1993), 147

3. V. Danek, M. Chrenkova, A. Silny, G.M. Haarberg and M. Stas, *Distribution of Phosphorus in Industrial Aluminum Cells, Canadian Metallurgical Quaterly, 38, 1999, 149-156*

4. R. Meirbekova, J.Thonstad and G.M. Haarberg, G. Saevarsdottir, *Effect of Current Density and Phosphorus Species on Current Efficiency in Aluminum Electrolysis at High Current Densities,* Light Metals 2014

5. E. Haugland, G. M. Haarberg, E. Thisted, J. Thonstad, The behavior of the phosphorus impurities in aluminum electrolysis cells, Light Metals, 2001, 549-553

6. T.E. Jentoftsen, *Behaviour of iron and titanium species in cryolite-alumina melts,* Dr.ing. thesis, NTNU Trondheim, Norway, 2000.

7. E.W. Thisted, *Electrochemical properties of Phosphorus Compounds in Fluoride Melts cells*, (Ph.D. thesis, Norwegian University of Science and Technology, 2003), 200-202

8. S Rolseth, *Tilbakereaksjonen i aluminiumelektrolysen,* Dr. Ing. Thesis, The University of Trondheim, NTH,1980

9. J Thonstad, TA Utigard, H Vogt, On the Anode Effect in Aluminum Electrolysis, Light Metals, 2000, 131-137

10. L Schuh and G Wedde, Removal of impurities from dry scrubbed fluoride enriched alumina, Light Metals 1996

11. P. Lossius and H.A. Øye, Removing Impurities from Secondary Alumina Fines