On-Line Chemical Analysis of Aluminium Metal in Primary Production Plants Using a Preparation Free Sample and Mobile Laser OES Analyser

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Abstract

A newly developed Directly Analysable, Sampling and Analysis System is presented allowing the aluminium smelter to acquire a chemical analysis safely and accurately within less than a minute and without waste on the pot room floor. An improvement over the current pot room practice of spooning and handling liquid metal is presented where the sample is solidified in the sampling device thus dramatically improving operator safety. A fast "chill" immersion sampler is applied to avoid elemental segregation and give a cool representative sample on stripping from the sampling device; this high-quality sample can then be directly analysed at the electrolysis pot location by an accurate mobile Laser Optical Emission Spectrometer. The analysis takes a few seconds, and the chemical analysis of the aluminium metal can be transmitted via Wi-Fi to the plant's process control system. It will be demonstrated that the important elements such as iron, silicon and sodium as well as copper are in good correlation with the conventional time-consuming lab results obtained via the normal sampling process.

Keywords: On-Line chemical analysis, Aluminium sampling, Laser OES, Improved safety.

1. Introduction

The safe and accurate analysis of the metal being produced via the aluminium electrolysis cell is of extremely high importance to the primary aluminium smelting industry.

The Hall-Héroult process has been used for over a century and is still the predominant production process for aluminium production; it involves the dissolution of aluminium oxide (Al_2O_3) in a molten electrolyte at 950–970 °C consisting of sodium cryolite (Na_3AlF_6) and some other minor composites. The process is governed by Faraday's law of electrolysis and under the influence of the direct current between the upper carbon anode and the lower carbon cathode, aluminium ions are driven towards the cathode and collect as the liquid aluminium pad below the liquid electrolyte.

The process is multivariate and requires careful control of the electrolyte chemistry, the electrical power input and the electrodes to achieve high efficiency and the correct chemical composition of the aluminium metal being produced.

Heraeus Electro-Nite supply the FiberLab® system which measures the electrolyte bath temperature, electrolyte liquidus, AlF_6 content in the electrolyte as well as allowing an alumina content prediction to be calculated thus giving information for controlling the electrolyte chemistry to achieve higher efficiency and productivity.

The chemistry of the aluminium produced is of utmost importance and can become contaminated by the chemical elements iron (Fe), silicon (Si), also accurate knowledge of sodium (Na) and copper (Cu) is required.

In normal industrial practice to sample the aluminium the sampling hole in the electrolyte needs to be broken open and cleaned manually by the operator; once done samples of the aluminium pad are taken from the bath usually by immersing a spoon, removing some liquid aluminium which has some electrolyte material mixed in due to the sampling; this electrolyte is removed by swirling the molten liquid in the spoon and decanting the electrolyte. This swirling puts the Na in contact with air, some of the sodium is volatilized, and is lost from the sample. Once the electrolyte is removed then the remaining aluminium can be poured into a steel or copper mould as shown in Figure 1, cooled and then sent to the smelter lab for Optical Emission Spectroscopy (OES) analysis.

Figure 1. Showing an operator pouring liquid aluminium into a mould at the smelter.

The current sampling practice needs to be carefully analysed and understood, during cooling from liquid to solid several phenomena can give rise to inaccuracies. Firstly, stratification occurs where during solidification solute elements like iron and silicon can be eliminated from the aluminium solid solution so higher concentrations are seen at the last place in the sample to solidify; this is well known and documented in aluminium foundry practises. Secondly it has been reported that for sodium [1-2] special care in needed to avoid volatilisation during sampling so fast cooling in a closed sampling chamber is preferable.

The primary elements that are required to be analysed for in the production of aluminium metal are iron and silicon. It can be assumed in well developed processes that the contaminants introduced from the raw materials are trace only however iron and silicon can be introduced by degradation of the smelter pot materials due to normal lining and anode wear with significant contamination of the aluminium metal being produced. Since the advent of copper cored cathode collector bars, the analysis of copper also became very important, especially as it allows to distinguish between anode and cathode degradation. Copper can also be added in known amounts to calculate the aluminium metal volume.

Anodes are consumed over a 28–32 day period where they are renewed once consumed to an minimum working point. Smelter size varies from 150 kA to the most modern plants being as high as 600 kA and pot numbers from 300 to 1500 per plant. Each pot has multiple anodes, for the older designs this is approximately 18 per pot and the larger higher current pots as many as 48, all of which require changing on a 3-4 weeks basis.

Anode design is based on a preformed carbon block connected to iron-based stubs which protrude into the anode, the connection between the stub and the carbon block anode is made using cast iron which also contains silicon. Due to the considerable expense of anodes in the electrolysis process it is important to push the anodes to their maximum lifetime which means that the iron stubs should be allowed to come as close as possible to the electrolyte bath but not be allowed to contaminate it; this requires extremely careful monitoring of the aluminium pad chemical composition. Once anodes begin to contaminate the aluminium metal due to the fact that the steel pins and cast-iron joining material become exposed to the electrolyte bath then the operators begin sampling the identified pot on a very frequent (multiple times a day) basis rather than once every few days. This high frequency requires fast analysis of the samples to allow remedial action to be taken on a timely basis and if necessary, the anode replacement schedule may need to be adjusted.

Silicon is also of importance for the smelter where possible sources can be the cast iron used to join the anode to the stub or the refractory lining of the pot which contains various sources of silicon containing refractory.

Copper can be added to the aluminium in a pot in very small amounts to allow the bath metal pad weight to be calculated but can also come from the cathode conductor bars if the carbon cathode has excessive wear.

Sodium content of the aluminium metal is reported to be very interesting for process efficiency where it has been shown to have a direct correlation to the current efficiency (CE) of the pot [1,2].

2. ALULAB and QUSAL Analysing and Sampling System

The mobile ALULAB LIBS spectrometer system is robust and capable of accurate operation in the primary smelter pot room environment. The modular design allows the system to be mounted on a trolley as shown in Figure 2, on a golf car or other mobile vehicle used in the pot room.

Figure 2. The ALULAB analyser mounted on an industrial trolley.

The sampling process involves simply push fitting the sampler onto a stainless-steel lance assembly, with minimal pre-heat the assembly is immersed quickly through the electrolyte and into the liquid aluminium pad as shown in Figure 3. The sampling operator exposure to the hazardous environment is minimised and most importantly there is no liquid aluminium being removed from the pot. Once in the aluminium metal the sampler capping burns away allowing the liquid aluminium to flow into the sampling chamber where it rapidly freezes avoiding segregation or loss of volatile elements.

Figure 3. Showing the sampler being immersed in the smelter pot.

The sample to sampler mass ratio is carefully designed to facilitate this fast cooling to achieve a homogeneous sample, limit surface reactions due to the instantaneously low temperature and allow easy operator handling from sampler to analyser.

The sampler immersion takes approximately 5 seconds, once the sample chamber has filled the lance is returned to a parking position on the analyser trolley where the sample is stripped by a simple crushing tool to remove the sample, the sampler body material is collected in a container below the crusher as shown in Figure 4.

Figure 4. Showing the filled sampler ready to be stripped.

The stripped sample can now be taken using light safety gloves to the sample holder on the analyser and the start sequence activated as shown in Figure 5. The analyser then conducts several cleaning burns with the laser on the sample surface to remove any minor oxide or dirt before commencing the analysis cycles. Total analysis time is less than 20 seconds and can be completed during the movement of the analyser to the next pot to be analysed; plant trials showed on consecutive pots it was possible to analyse each pot in less than a minute. Once the analysis is complete then the data can be automatically uploaded via Wi-Fi to the plants control system.

Figure 5. Showing the clean and homogeneous sample being loaded into the analyser.

The ALULAB plus QUSAL sampler allow the smelter operators to accurately sample, analyse and proactively react to the aluminium chemistry in a fraction of the time and complexity the conventional sampling and lab analysis process takes. This is extremely important where unforeseen issues occur within the pot which could be premature anode failure due to cracking and higher than normal oxidation or anode effects which cause the steel stub and cast iron to become exposed to the bath faster than expected; this allows the operators to safely maximise lifetimes and achieve the required metal quality.

The sampler components are compatible with the electrolyte so can be simply tipped into the pot once the sample is retrieved leaving zero waste from the sampling process.

2.1 System Accuracy

The ALULAB and QUSAL system have recently completed significant industrial testing on a number of primary aluminium smelting plants where its ease of operation, speed of analysis and dramatically improved safety have been verified to show a substantial improvement for aluminium metal analysis in the pot room environment.

The ALULAB analyser is rigorously calibrated using Calibrated Reference Materials during manufacture. The system itself is designed to remain stable during operation and requires only infrequent checks and minor maintenance to ensure system accuracy during industrial operation.

Figures 6–11 show the ALULAB calibration and accuracy against Certified Reference Materials (CRM). It should be noted that there are limited CRMs available for sodium (Na) metal in an aluminium matrix however tests at an industrial smelter show a good correlation to the standard samples and lab values with the QUSAL sample showing a slightly positive offset at approx. 10 ppm due to the fast cool and avoidance of sodium volatilisation, thus giving a more accurate value. Work is ongoing to improve this calibration and quantify sodium's effect on Current Efficiency.

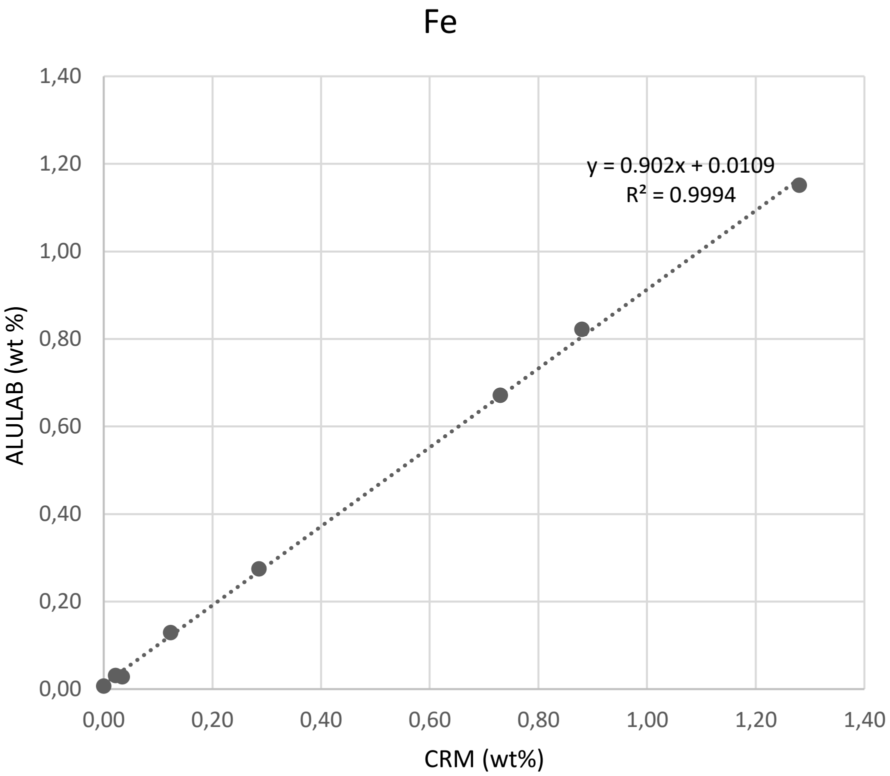

Figure 6. Graph showing ALULAB calibration against the CRM for iron.

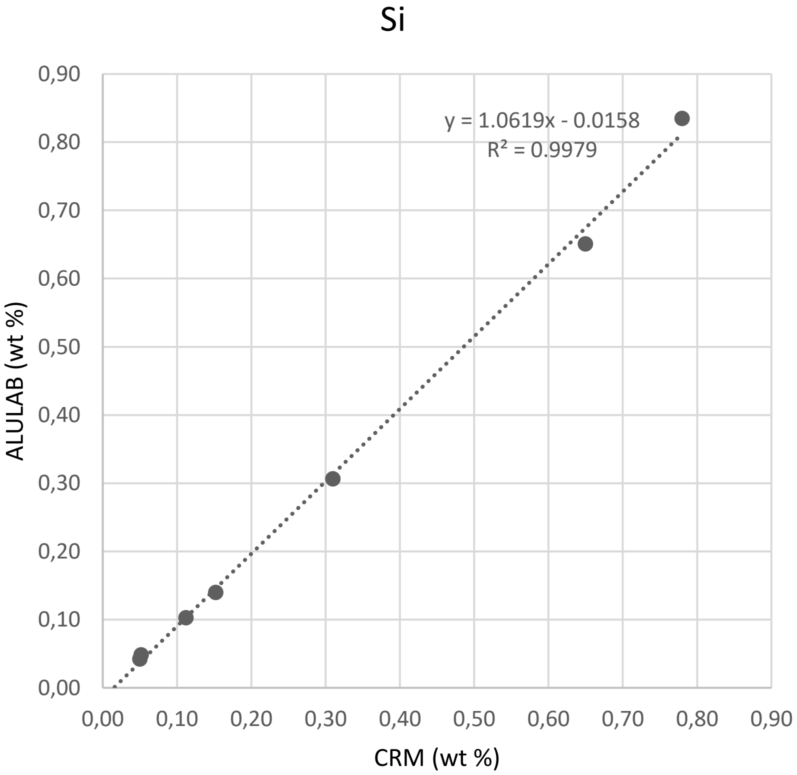

Figure 7. Graph showing ALULAB calibration against the CRM for silicon.

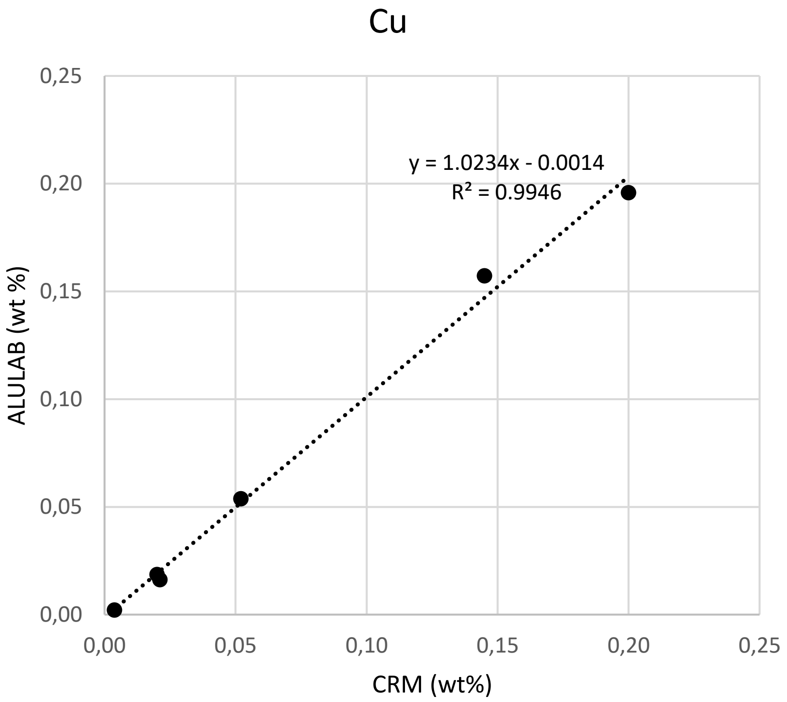

Figure 8. Graph showing ALULAB calibration against the CRM for copper.

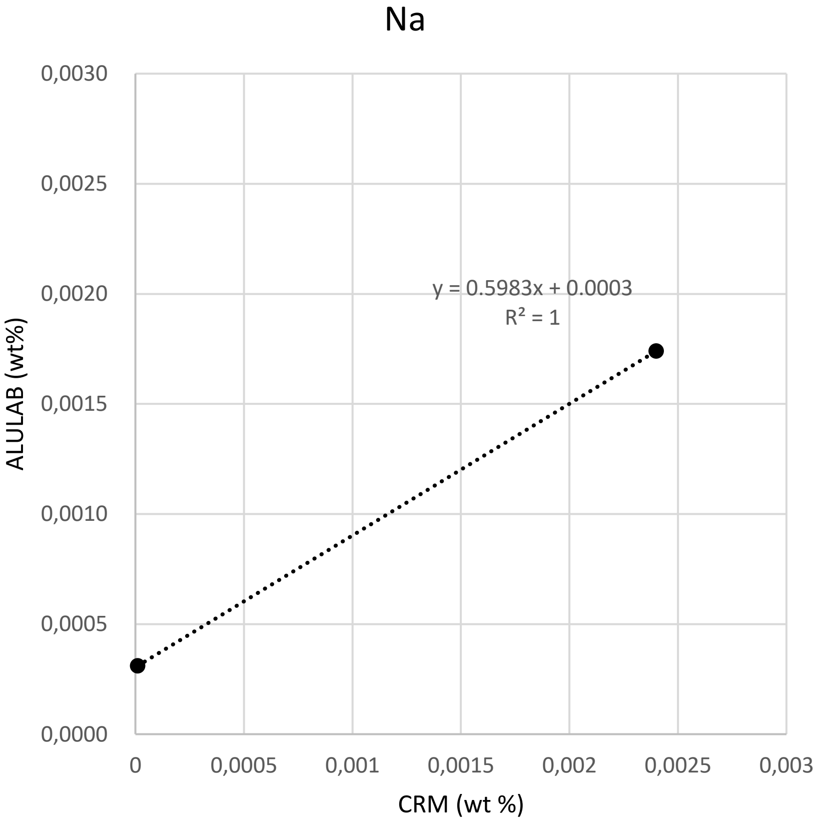

Figure 9. Graph showing ALULAB calibration against the CRM for sodium.

The detection limits of elements as shown in Table 1. are significantly lower than the minimum concentrations for all the elements of interest analysed in the aluminium metal of a smelter electrolysis production cell.

Table 1. Limit of detection of elements for ALULAB.

Element	Limit of Detection (ppm)
Iron (Fe)	68
Silicon (Si)	78
Copper (Cu)	24
Sodium (Na)	4

Figures 6-9, show the accuracy achieved by the ALULAB LIBS analyser on Certified Reference Materials, Figures 10 and 11 then show that this performance is also achievable in the industrial environment when the analysis is conducted on the QUSAL samples. These results are shown to be in very good correlation with the industrial spoon sampled metal which has been prepared by milling and then analysed by a conventional lab spark OES analyser. These results have now been verified in 3 separate large scale industrial smelter trials and industrial adoption is now on-going.

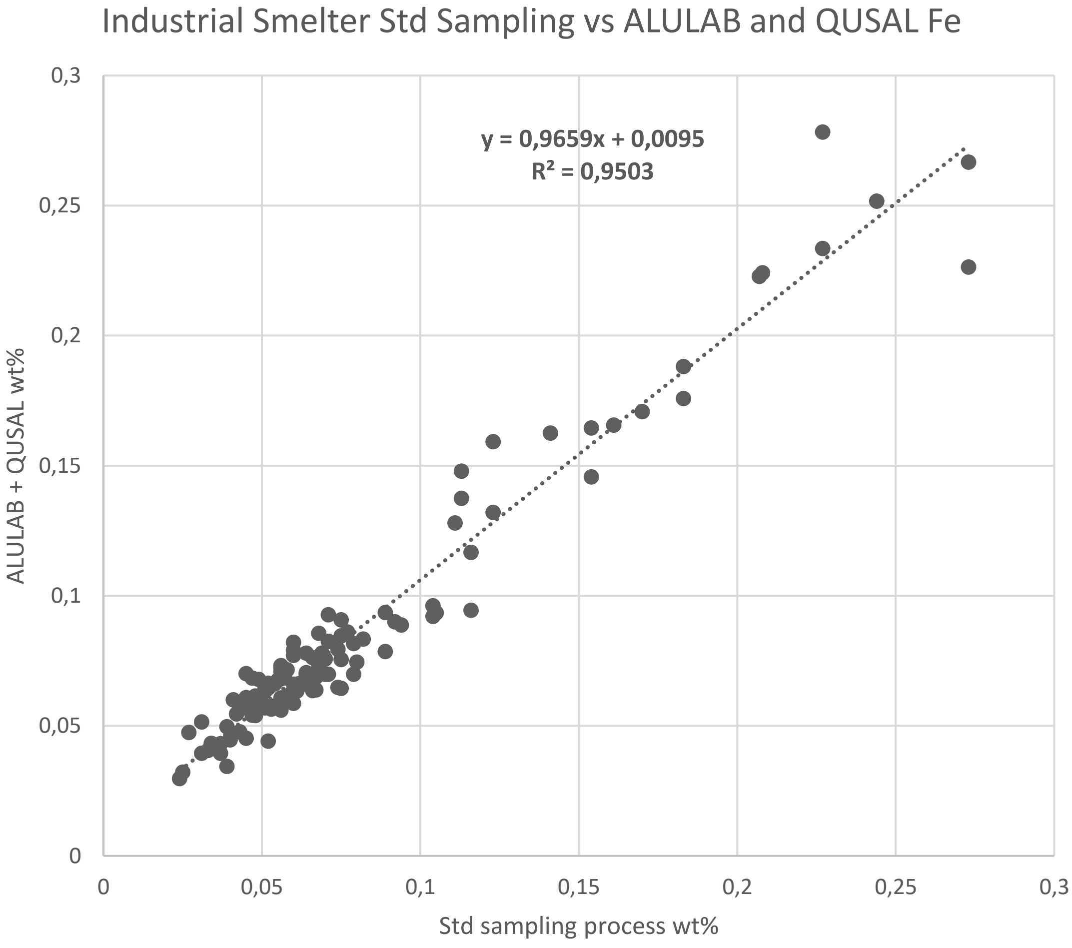

Figure 10. Graphs showing industrial plant results vs QUSAL and ALULAB for iron.

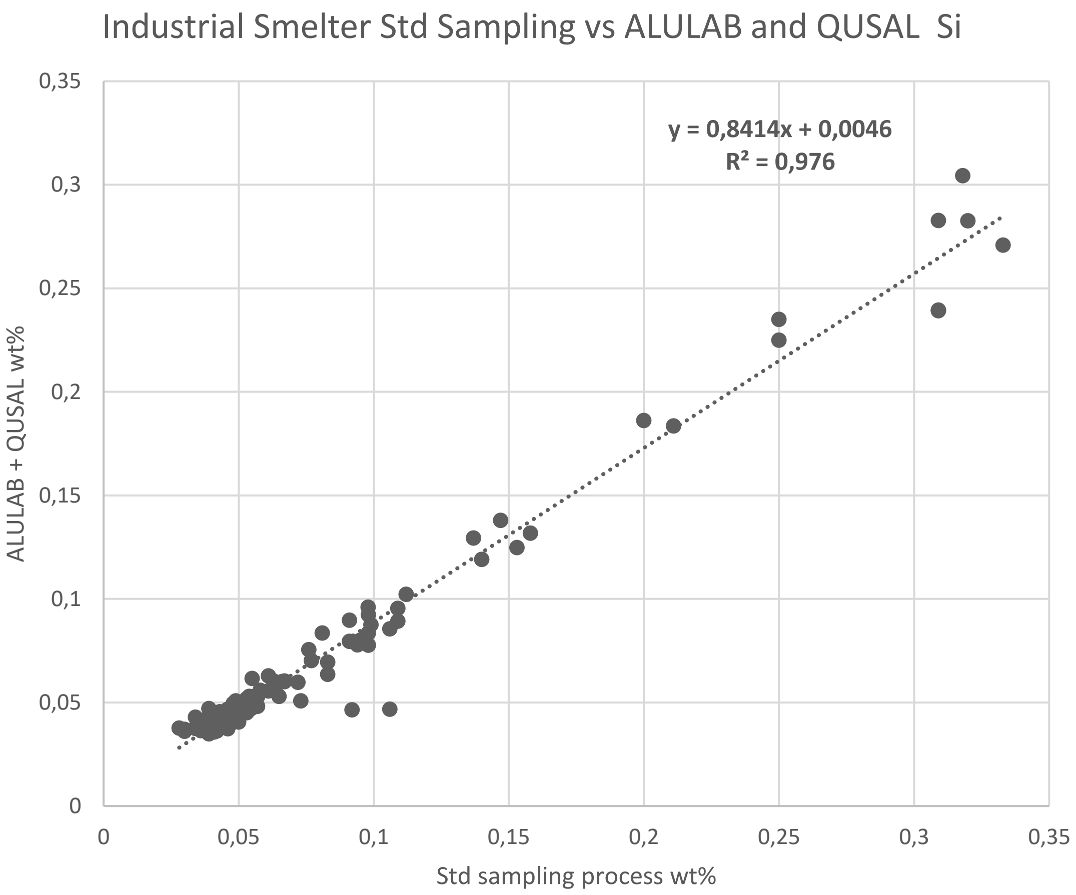

Figure 11. Graphs showing Industrial plant results vs QUSAL and ALULAB for silicon.

3. Conclusions

QUSAL is a new sampling device which has been developed for sampling aluminium metal in the primary smelter environment, QUSAL delivers considerable benefits over current practices. Along with QUSAL the ALULAB mobile analyser allows the sample to be analysed in a matter of seconds giving real time information. These benefits can be summarised as follows:

- The QUSAL sampler is an immersion sampling device where the aluminium sample is acquired in a closed environment which excludes contamination of electrolyte material and removes the operator from exposure to both liquid aluminium and electrolyte dramatically improving safety compared to the conventional spooning of liquid aluminium into a separate mould.
- The QUSAL sampler obtains a sample which is homogeneous and without segregation or volatilisation of important elements due to the extremely fast cooling rate removing sample irregularities, also the sample surface is contamination free with minimal oxidation so requires no preparation before OES analysis.
- The QUSAL sample once removed from the sampling device is cool and can be directly inserted into the ALULAB analyser for rapid analysis on the smelter pot room floor.
- In conjunction with the QUSAL sampler the ALULAB Laser Induced Breakdown Spectroscopic analyser has been developed to be mobile, accurate and robust to allow the QUSAL sample to be analysed withing seconds at the sampling location avoiding the time delays associated with conventional laboratory sample analysis. This instant analysis

offers significant improvements for monitoring pots where anodes of even pot linings are at end of life and impact on process and product quality.
- Initial field trials have shown a significant interest in the QUSAL and ALULAB's ability to remove the sampling inaccuracies and measure the sodium content of the aluminium metal. A detailed study is ongoing to relate this to Current Efficiency which will allow the smelter to detect process outliers and correct the process conditions without a significant deterioration of the pot performance.
- The QUSAL plus ALULAB system is cost effective as it eliminates the preparation step and a significant amount of the lab cost as the operator who takes the sample on the pot room floor also conducts the analysis. Initial field trials are ongoing and are proving this to be the case. A detailed analysis will be presented at a later date.

4. References

1. Asbjorn Solheim, Sodium in Aluminium as a Cell Performance Indicator: A Quantitive Framework. *Light Metals*, 2017, 633-639.
2. Lukas Dion and Paul Desclaux, Fundamental Loss of Current Efficiency During Aluminium Electrolysis and Its Correlation with Sodium Content Dissolved in the Aluminium. *Light Metals*, 2024, 630-638.