

## Process optimization by real time analysis of liquids' composition in Metal & Mining

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The XRF method, with a long-proven track record, is one of the most common analytical techniques for elemental measurement in the metal & mining industry. The technology offers high safety, low OPEX, with high versatility and availability, covering the whole range of concentrations, starting from ppb levels (in the range of 0,00001%) up to 100%. The success of the technology lies in the fact that it can be applied to most of the periodic table, can be used on both solids and liquids, gives real time measurements on the spot, is non-destructive for the sample and does not consume chemicals. In addition, the technique often does not require high skills to be applied, provided that the methods for the XRF-analysis are set up correctly by means of a suitable calibration. Among these benefits, one of the main reasons to elect this technique over others available, is the “speed of response” that can give a feedback within seconds of what is taking place in a hydrometallurgical process, indicating for instance a reaction occurring or not occurring, a side reaction rate increase, reagents being depleted or the formation of unwanted species leading to an emergency situation. Process Engineers and operators often require knowing step after step what is going on inside a reactor, in order to be able to intervene as early as possible. Today, thanks to a multi-element analysis by XRF, fortunately this is possible.

Alike any test technique, sample preparation is crucial, thus measuring on representative samples is key to control process optimization and obtain real-time feedback on metals and other elements, in order to improve quality, planning, safety, to prevent unknown losses and reduce use of excess chemicals. This brings about not just an economic benefit, but also an overall improved environmental balance. Also, small improvements at every step of an integrated hydrometallurgical process, at the end may result in large quantities of revenues for increased throughput, improved product quality, reduced reagents, but it will also reflect into a better use of resources, reduction of raw materials used, decrease of emissions and waste to be disposed of. For instance, a more efficient water treatment process will save more metals, while releasing a waste solution with a lower impact to the environment.

When an ore is concentrated into a metal containing matte, it must undergo a leaching stage that will dissolve some elements and leave others in the solid form. Having a thorough control of all the elements present is not trivial, but it is key to optimize all the following refining stages, since ores are never constant in composition and from time-to-time unwanted elements may exceed the limit without notice. This is a perfect case in which the “speed of response” and the “high accuracy” of an online analysis can play an important role for the Metal & Mining processing industry. In this paper, the authors introduce their own “case study”, made by the world renown and leading manufacturer Glencore, at its Nikkelverk plant in Norway, that has made use of the “C-Quand online XRF analyzer” fabricated by Hobré Instruments, a world leading manufacturer of analyzers and sample conditioning systems. The online XRF analyzer is employed for the control of the critical leaching phase of the Ni-Co-Cu matte, substituting a much more complicated and costly analytical technique that used to make use of a lot of reagents and a large equipment. In addition, the technique used before required a substantial amount of human workforce to cope with maintenance of the systems. The results, challenges and the improvements of the first two years of utilization of the online XRF analyzer will be shared, showing that Process Control cannot live without proper measurement, thus measurement on representative samples is truly the heart of processes.

### Introduction

Every human activity requires resources, thus it is particularly important to optimize their use, as their depletion is a vital global concern that affects the life of every individual, especially when they are not renewables. Beside scarcity, society faces acquisition difficulties as mining is not evenly spread out all over the world. For instance, the “Earth Overshoot Day” is just an example of one of the many parameters and indicators showing how we are going in the wrong direction by depleting the “projected allocated resources” of a given year, in a shorter and shorter time, year after year. In metal processing field, every step poses important optimization opportunities for its environmental and economic impact. The practical approach of resource management is particularly well suited to the metal & mining industry, which have much scope to adopt a sustainable approach to their activities. Besides considering the environmental and collective impact of their operations, metal & mining companies ought to take steps to minimize negative effects<sup>1</sup>, share best practice (often referred as best available techniques<sup>2</sup>), reuse resources used during processing, minimize the environmental impact and reduce waste.

### Optimising mining performance and Minimising “wasted” resources

Mining as an industry creates much waste, including depleted rock, gaseous emissions, sludges, mine water and spent water from hydrometallurgical processing. Some of these streams can be reused, either within the same production or repurposed elsewhere.

For instance, waste rock can be used as backfill as landscaping material or in road construction, while the sludge can be used in pigments. Other by-products can be re-used for making construction materials (e.g. bricks or in cement kilns), resins, glass and glazes, in agroforestry, or as part of the wastewater treatment process<sup>3</sup>.

There are also other waste streams related to the subsequent stages of smelting, up to the final refining steps of the minerals. Considering the concept of the “waste hierarchy”, the first step to take to minimize resource use is “reducing the amount” used. One way to do this is to optimize the leaching and extraction processes, in order to “leave behind” as little as possible of the key metals contained in the ore to be processed. For instance, if in an ore containing 2.0% cobalt the froth flotation process would leave behind a content of 0.1%-0.5%, it would mean that 1-5 kg of Cobalt per metric tonne of ore would end up in the waste stream. This would likely cause a “contamination” problem to the secondary uses mentioned above, but in terms of resources, it means that 5-25% of the contained cobalt does not get extracted. To understand the impact, it can be considered that in order to produce 1 metric tonne of cobalt, in this example 53-67 t of ore would be required. Comparing this to the 50 t required if the process was 100% efficient, it is clear that 3-17 extra metric tonnes need to be processed, with all the impact related. Multiplying this amount by 10 kt of cobalt produced per year by a large producer, would mean 30-170 kt of extra ore that ends up in the waste stream, containing an equivalent of 30-850 t of Cobalt!

In order to optimize every step of the process, it is important to closely monitor the chemistry of the reactions occurring and this can only take place effectively through a continuous process sampling and control. The continuous analysis, active 24 hours a day, minimizes the dependence on operator's intervention, as the process disturbances are rarely predictable.

### Continuous process analyzers for hydrometallurgy

The online analysers traditionally used to control hydrometallurgy in real time include techniques like photometric analysis. In recent years new analytical equipment like titrators and voltametric analysis have been implemented to improve the process control. Every technique has been developed to solve some problems, but some of them bring real challenges for their deployment. For instance, the photometric analyses require several stages to measure different elements since each photometer only measures one element at the time and a large room for the equipment. At Nikkelverk, the photometric analytic method for Ni, Co and Cu reported in g/L is simple, measuring the colour of the solution and relating it to the concentration via Lambert-Beer's law without adding any chemicals. The main problem is the need of dilution of the process solution prior to analysis. The dilution is not accurate and can therefore give poor results. For trace analysis of these elements, chemicals need to be added to enhance the samples response when measured.

In general, titrators may require a long time before the titration is complete and if the reaction is contaminated by other species, results can be altered. Inductively Coupled Plasma (ICP) is probably the most widely used technique in benchtop laboratory equipment, however the difficulty to apply it for a continuous process control lies mostly in the sample preparation that needs to be appropriately diluted based on the actual concentration. Finally, the XRF technique, which is the main technique discussed in this paper, in short requires a compact analyzer, no need of reagents, does not consume or alter samples, does not need dilution and can work on a very extended range, from sub ppm to 100 wt%. The specific details are discussed in the next section.

### XRF technique

X-ray fluorescence (XRF)<sup>4</sup> is an analytical technique that can be used to determine the chemical composition of a wide variety of sample types including solids, liquids, slurries and loose powders. It is also used to determine the thickness and composition of layers and coatings.

XRF spectrometry is a non-destructive analytical technique used to obtain elemental information from different types of materials, as it can analyse elements from beryllium (Be) to uranium (U) in concentration ranging from sub-ppm levels to 100 wt%. It is employed in many industries and applications including: cement production, glass production, mining, iron, steel and non-ferrous metals, oil & gas, polymers and related industries, forensics, pharmaceuticals, healthcare products, environmental, food and cosmetics.

XRF analysis is a robust technique, combining high precision and accuracy with straightforward, fast sample preparation. It can be readily automated for use in high-throughput industrial environments, while providing both qualitative and quantitative information on a sample. The technique is so versatile that it is often used for rapid screening (semi-quantitative) analysis too.

XRF is an atomic emission method, similar in this respect to optical emission spectroscopy (OES), ICP and neutron activation analysis (gamma spectroscopy). Such methods measure the wavelength and intensity of ‘light’ (X-rays in this case) emitted by energized atoms in the sample. XRF makes use of X-ray radiation to eject an electron of the measured element from the inner orbit; the vacant place will be taken by a higher orbit electron, under emission of a very specific wavelength of X-ray radiation: fluoresce (Figure 1). The amount of energy coming from the sample in this wavelength has a linear correlation with the concentration for a short concentration range. The enhancement and absorption effects make the

calibration itself more complicated, however this can be corrected by mathematical models in the instrument software.

An X-ray tube produced irradiation by a primary X-ray beam, causing emission of fluorescent X-rays with discrete energies characteristic of the elements present in the sample (Figure 2).

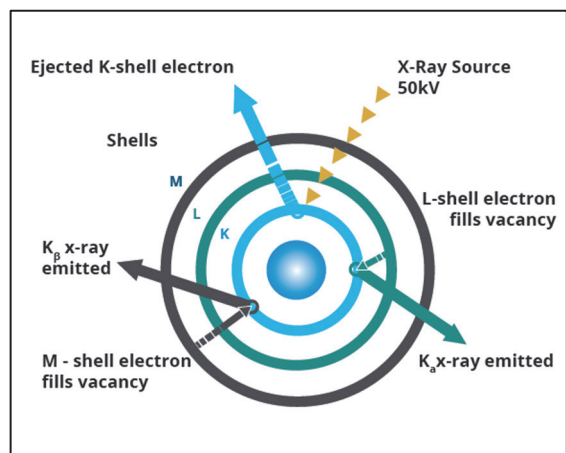


Figure 1. X-Ray fluorescence principle.

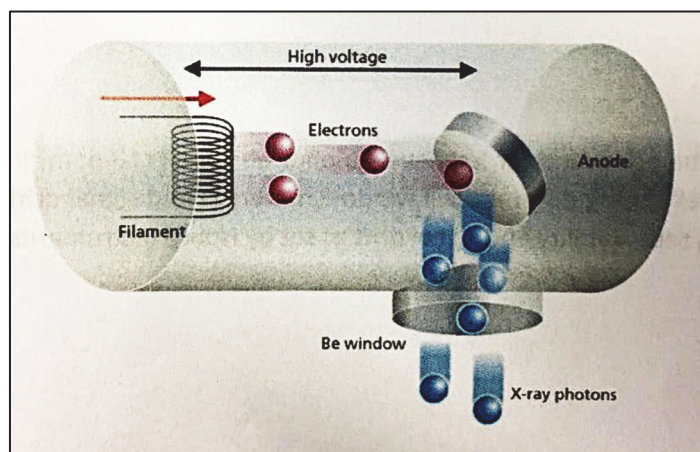


Figure 2. X-Ray basics.

A radiation source stands at the basis of all spectrometers, together with a sample and a detection system. The technology used for the separation (dispersion), identification and intensity measurement of a sample's X-ray fluorescence spectrum gives rise to two main types of spectrometers wavelength dispersive (WDXRF) and energy dispersive (EDXRF) systems. For the purpose of this paper, the latter will be considered.

In EDXRF spectrometers, the X-ray tube acts as a source, it irradiates a sample directly and the fluorescence coming from the sample is measured with an energy dispersive detector. This detector is able to measure the different energies of the characteristic radiation coming directly from the sample. The detector causes a separation (called dispersion) of the radiation from the sample into the radiation from the different elements present in the sample. Thus on the detector X-rays are converted to electron clouds, proportional to the energy of the X-ray. The clouds "drift" down a field gradient to the anode, and get collected to charge a capacitor (figure 3).

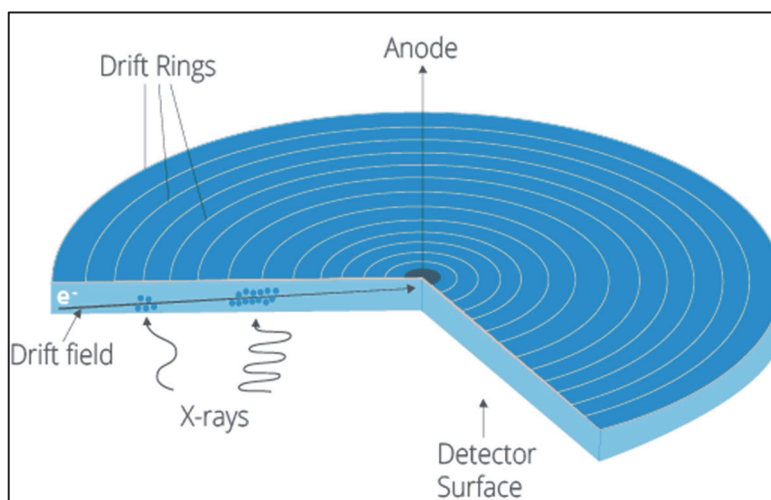


Figure 3. Energy dispersive detector<sup>5</sup>.

### Glencore Nikkelverk process

Glencore Nikkelverk is the biggest nickel refinery in the western world exporting 100% of the production, primarily containing nickel, copper and cobalt. Around 50 product variances are exported to markets all over the world from the Nikkelverk. A characteristic of all the products is high quality and the purity of the finished metals are amongst the highest in the world.

Since 1910 Nikkelverk has refined, produced and exported nickel and other metals from the production plants in Kristiansand. Product development has been necessary to satisfy the needs of the customers. Its environmental, energy and process technology has made the Nikkelverk plant one of the most effective and technologically advanced refineries in the world. The Nikkelverk process begins by crushing the raw material into a fine powder and transporting it to the chlorine leach plant. Here the metals in the raw material are separated by addition of chlorine in hydrochloric acid. The separated streams are then sent to different processing areas for purification and refining. Various process areas treat gaseous, liquid and solid materials (see figure 4). From these areas, the different products are sent for finishing treatment, cutting, and packaging before they are shipped out to the world market.

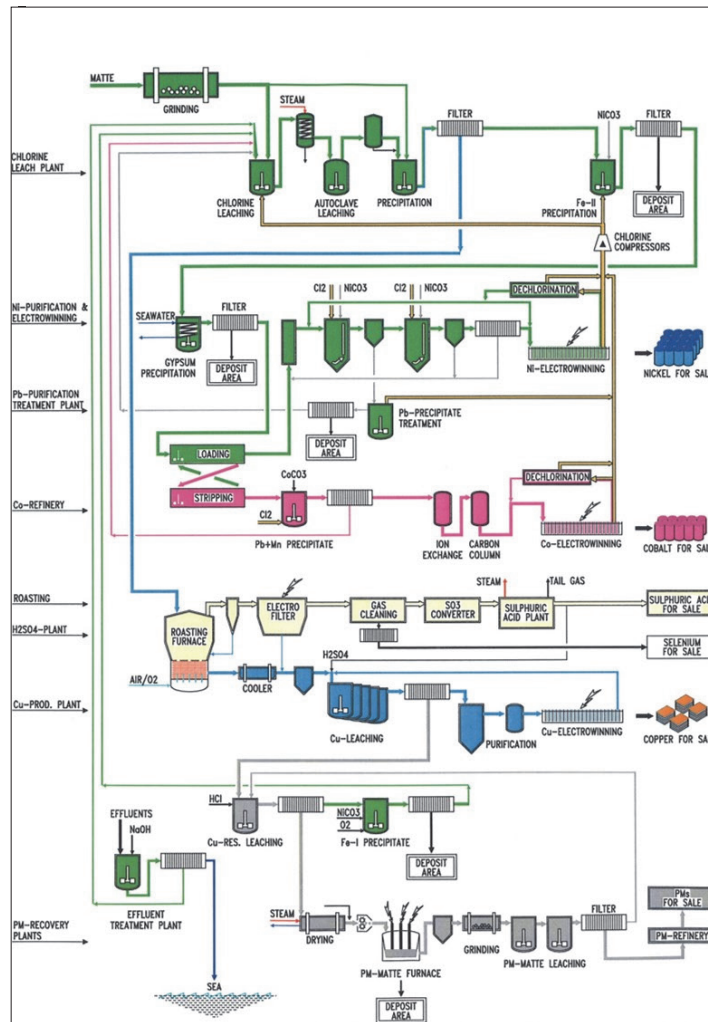


Figure 4. Flowsheet of Nikkelverk's process.

### XRF analysis applied to leaching

The first step for treating the extracted ore is generally a froth flotation process that concentrates the metals contained. Afterwards, the concentrate is transformed in a sulphide matte. This matte is then transferred to the hydrometallurgical section, whose first step is leaching, which is the process of dissolving a solid into a suitable solution, in order to allow the following steps entailing purification, precipitation and so on, until final refining.

In order to optimize the leaching process, it is required to run a real time analysis to the process, especially because the matte coming from an ore can be fairly variable in composition. This continuous analysis can be run through XRF technology, as this is the most viable technique available, given its versatility and speed of response. For this reason, after many years of successful use of photometric techniques, *Glencore's Nikkelverk* plant in Norway has decided to switch to XRF for the control of the critical leaching phase of the Ni-Co-Cu matte. The selected analyzer for this purpose is a "C-Quand" fabricated by *Hobré Instruments*, a world leading manufacturer of analyzers and sample conditioning systems. The main advantages of this analyzer are:

- Multi elements simultaneous analysis
- Ability to handle the whole pH range
- Analyse a wide range of concentration without consuming the sample
- No dilution of sample
- No need of reagents
- High precision measurement
- High stability measurement
- It can be used with both aqueous or organic solutions

### Calibration of the instrument

Before being able to run a sample into an analyzer, it is important to calibrate the instrument for the given elements and range to check. XRF technology makes no exception in this regard. Thus, the calibration takes into account as many variables as possible, but most importantly:

- Primary elements required for the process
- Secondary elements (less important) for the reaction
- Contaminants (e.g. elements that affect X-Ray absorption)
- Matrix (e.g. aqueous solution, organic solution)
- Solid particles possibly present

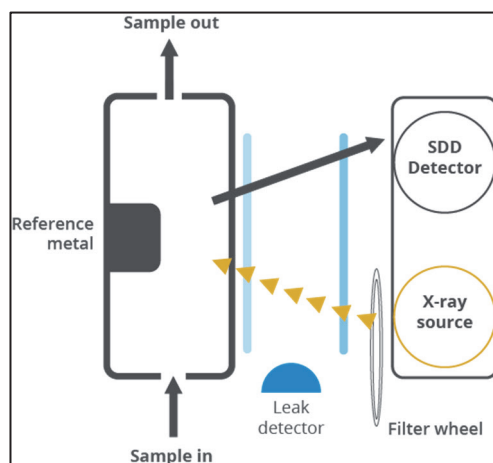
In general, all elements influencing the calibration need to be a part of the calibration setup. The calibration allows the build-up of a “calibration curve”, that is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known [concentration](#)<sup>6</sup>. Thus, the known samples must be representative and take into account the concentration ranges for the items enlisted above and assess the correlation of as many variables as possible. The ideal situation entails a linear relationship where the curve can be approximated to a straight line, however often this is not the case, such that calibration could need to be split for the different applicable ranges and limits could be introduced to curb the possible combinations.

Prior to calibration, it is important to be aware of matrix effects and possible overlap corrections for each element as well as pile-up signals from the detector which can distort the real analytical content of the elements to be analysed. In this specific case study, the calibration of the Online XRF at Nikkelverk was done with “inhouse” calibration samples which are mainly process samples from different part of the plant. Actual process samples are not suitable as calibration samples, since they are unstable and start to precipitate when cooled to room temperature. Therefore, the “inhouse” calibration samples are more diluted than the actual process samples to be analysed. Furthermore, synthetic calibration samples from pure chemicals, called primary standards, were also implemented into the calibration to cover the whole concentration range.

The major elements in all calibration samples were determined on a WD-XRF-instrument (Axios) at the main lab. The minors and trace elements were determined with ICP and AAS. The calibration is made by using theoretical alphas corrections for all fourteen elements in the calibration. Water is used as a “balance-element” in the calibration model. This calibration model gave the best calibration for a wide concentration range and was found to be suitable for all the actual process solutions.

### Test run

Once the calibration has been set, unknown samples can be analysed making use of the calibration curves, to analyse the elemental composition.



**Figure 5. Hóbré C-Quand XRF analyzer cell layout.**

Figure 5 shows the Hóbré C-Quand XRF analyzer cell, indicating that there is a continuous flow through the cell, subject to a continuous X-Ray irradiation used to measure the sample continuously. The analyzer then displays a “moving average” over a definite timeframe, so that each result is high in accuracy and repeatability.

During test run, the XRF-system needed to be adjusted to fit the needs of the Nikkelverk’s process solution. For example, the flow cell, where the process solution is exposed to X-rays, was redesigned to make it deeper fulfilling the concept of an “infinite thick sample”. Furthermore, the Hóbré’s Online XRF instruments uses normally a reference metal (for instance Zirconium) as a part in the flow cell to be able to correct for drift in the instruments. This reference metal had to be removed for Nikkelverk’s purposes since its signal during measurement of the calibration samples interfered with the calibration model. Drift correction has therefore been done with a Zirconium containing solution added manually to the system.

After adjustment of the Online XRF system and successful calibration, another issue to be solved was the injection of the samples to the instrument. The used layout installation analyses three process streams sequentially. Therefore, a sample extraction system for each process stream is needed ensuring that the “actual” process composition is introduced into the analyser at all time giving real-time results. The amount of particles in these solutions was initially assumed to be minor, but after a few months of tests it was revealed to be more substantial. The number of particles can vary in relation to events in process steps prior to the analyser. With the valves initially installed in the sampling system, clogging was occurring frequently and it disrupted the continuous measurements. These valves were exchanged with so-called “slurry valves”, able to cope with particles in the process solution, thus the clogging problem was solved and it was ensured a more stable operation of the complete analytical system.

Since the process solutions contain at times chemical components which can deposit over time on equipment part like tubes, valves or in the flow cell, a frequent washing cycle of the sampling and XRF-system is necessary. This has to be done manually by the operator for the current time-being and is planned to be automated in the future.

### Processing of data

Currently, both the photometric analyses as well as the Online XRF analyser are running parallel at the plant. This gives the opportunity to compare the two different systems with each other.

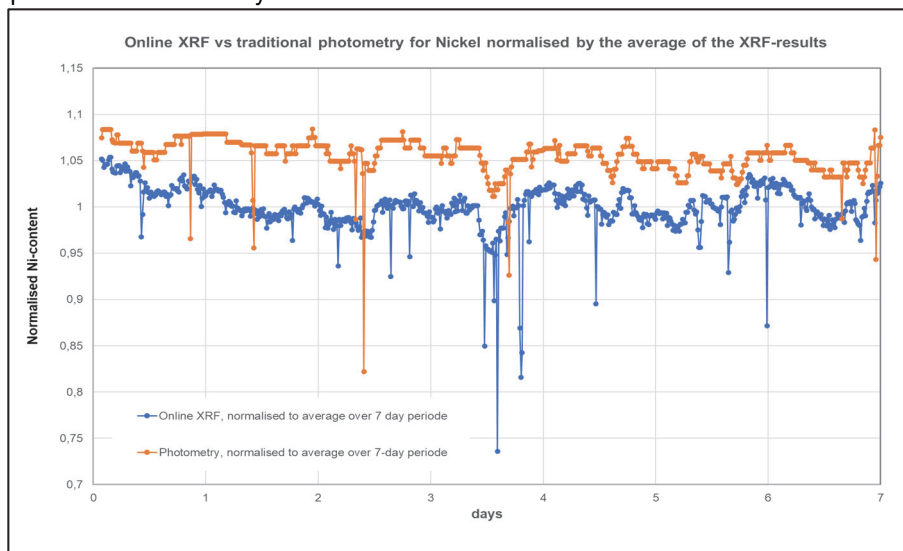


Figure 6: Plot of Ni results, normalised towards 7-day average of XRF-analysis, for both XRF and photometry.

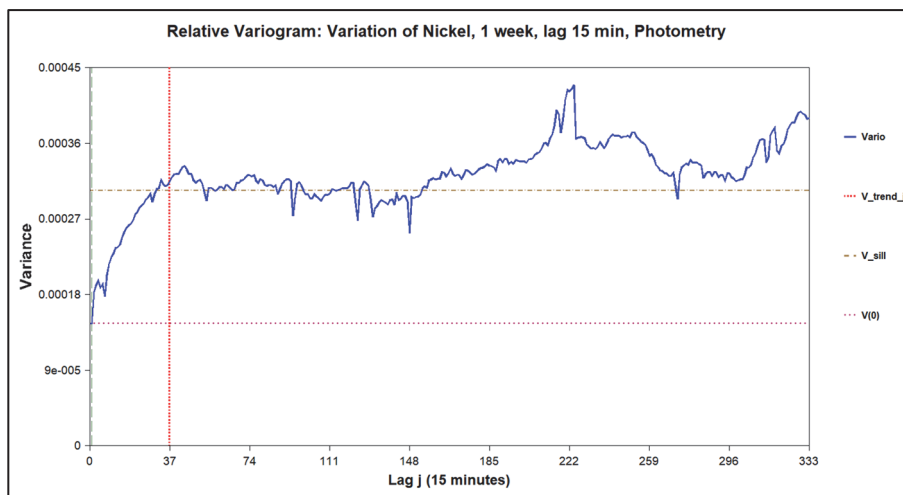


Figure 7: Relative variogram of Nickel measured by the Online XRF

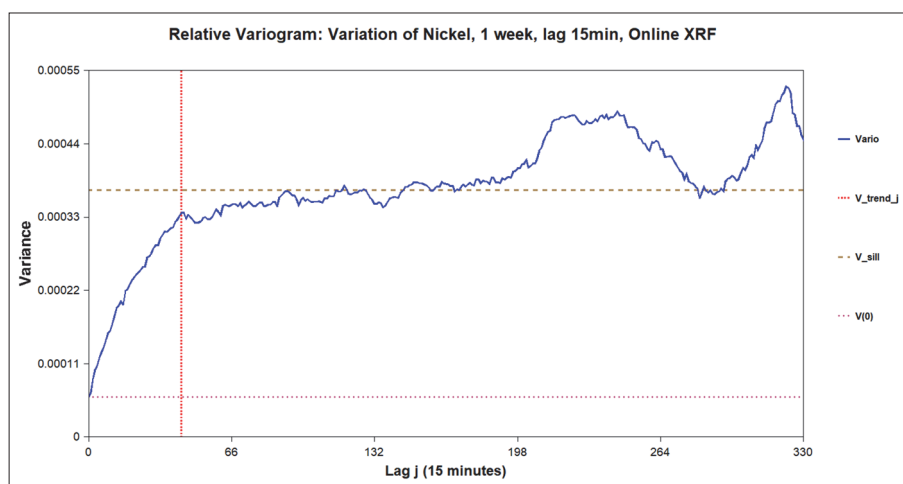


Figure 8: Relative variogram of Nickel measured by photometry

Figure 6 clearly shows a bias between the traditional analysis, photometry, and the newly established XRF-method. However, the trends of the two separate curves are similar. The XRF-system transfers its data to the steering system via Modbus. The photometric measurements are transferred via an analog system and filtered, as can be seen from the graph, with a certain threshold. The drops in concentration during the 7-day period are due to loss of sample towards the instruments, and for the XRF-system the washing cycles with acidic solution.

To determine the variance of the analytical systems, though limited for the photometry due to filtration, one can apply a variographic analysis for both series as shown in figures 7 and 8.

**Table 1: Comparing the relative variance of the measurement systems to the relative total variance of the process**

| Extracted key variables                  | Online XRF Nickel | Photometry Nickel |
|------------------------------------------|-------------------|-------------------|
| $V_{(0)}$ – measurement system variation | 0,00006           | 0,00013           |
| $V_{(sill)}$ – total variation           | 0,00037           | 0,00030           |
| Ratio in % for $V_{(0)}/V_{(sill)}$      | 16                | 44                |

Variance table

As presented in table 1, the measurement system variation presented as  $V_{(0)}$  is rather small compared to the total variance of the process regarding the Online XRF analyser. The photometric method shows a higher measurement system variation compared to the overall total variance though it would be expected to have a rather low  $V_{(0)}$  due to the similar values at times in figure 6 for the photometric measurements. Nevertheless, if the reason for this discrepancy is due to presentation of  $V_{(0)}$  or the filtration of the photometric data by the setup in the data transfer system, the relative total variance is in the same order of magnitude. The improved data transfer by Modbus for the Online XRF analyser will give a better insight for the process operators.

Looking at the ratio between measurement system variation and total variation, reported to be 16% for the presented 7-day period, this is in accordance with the demand that measurement systems under control should contribute close to or below 10% to the total variance<sup>7, 8</sup>. Since the Online XRF system still is above 10%, this can be explained with the lack of an automated acid rinsing procedure and that the calibration can be further refined.

### Reliability of measurements

As for many analytical systems incorporated on-, in- or at-line, the system itself has a high precision when tested in controlled conditions. However, presentation to process solutions changing over time as well as how the samples are introduced to the analytical system is a major challenge. The reliability of the measurements is primarily influenced by the feasibility of collecting representative samples, and by the sample matrix (liquid totally or partially free from particles). In this specific example, as samples normally contain some solids, it has been necessary to design a sample conditioning system including slurry valves that can cope with the solid particles present. In addition, in order to keep the lines free from obstructions, they have been subject to a washing from the sample take off point to the analyzer inlet, every 8 hours, using a warm acid solution. This routine has increased the uptime to over 95%. Future improvements will entail an automatic acid rinse routine.

### Advantages of continuous measurement in Nikkelverk's hydrometallurgical process

Since the 1970s, Nikkelverk has applied online analytical systems in the hydrometallurgical process to improve the ability to control the processes in real-time. At that time, it was not possible to purchase online analytical equipment easily from suppliers. Therefore, the systems still running at Nikkelverk were setup by very skilled inhouse resources enabling Nikkelverk to run its processes in a much more precise manner and counteract fast upcoming situations. However, the systems installed at that time require constant maintenance and consume partly vast amount of chemicals. As mentioned in the previous section, one system analyses one element at a time which results in a massive instrument park to be maintained today.

Therefore, current commercially available systems like the Online XRF have been implemented at Nikkelverk, reducing the use of resources. As for the implementation of the Hóbré Online XRF analyzer, the use of chemicals for analytical purposes is redundant, leading to a safer work environment for the operators. The maintenance work is reduced from currently nine photometric to one XRF instrument, reporting simultaneously results for 14 elements for each of the three process streams. As the XRF instrument is running stable with the present washing routines, the results reported are extremely helpful for the operation of the process. Since components like sulphate can now be reported in real-time to the shift operators, balancing of the process has become more stable, improving quality, saving resources and improving the overall safety.

### Conclusions

In this paper they were discussed the advantages of the XRF technique for the continuous monitoring of hydrometallurgical processes. A special focus has been given to the leaching stage of Glencore's Nikkelverk plant, for which it has been employed Hóbré Instruments' C-Quand XRF analyzer, customized according to the plant's special needs and requirements.

To get the Online XRF analyzer to its optimum, further improvements are planned regarding the automated washing procedure and an even more fine-tuned calibration. The outcome of the first 2 years of operation has shown that application of modern analytical equipment enabling multielement analysis is the ideal tool to reach improved process control and reduce use of resources, while providing a safer, more reliable and "requiring less maintenance" instrument to the operators. Though the development of XRF-methods and the need to customize the sampling system to fit-for-purpose tool was time-consuming, it is less time consuming than running and maintaining the old analytical techniques employed. Thus, Glencore Nikkelverk's result so far show clear benefits for the long run.

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