Understanding sampling variation – a vital aspect of industrial research experiments

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Abstract: Industrial research experiments are conducted in various scales in the mining industry. regardless of the experimental purpose, sampling and analysis is normally always a part of the experimental process to collect necessary data. However, in order to ensure that the experiment will enable valid conclusions, the understanding and minimisation of sampling variation is crucial. Two effective methods for evaluation of sampling variability in any process sampling situation are the duplicate and replication experiments. The application of sampling experiments in the early phases of a demo- or pilot-scale experiment is an effective way to both understand the total measurement system variability, as well as the possibility to improve sampling methods if the sampling variability is deemed too high to enable representative results to use for experimental evaluation. LKAB is an iron ore mining company in the north of Sweden where experiments are conducted in all parts of the process value chain with regularity. In the current state of the world, encountering more and more threats to our global climate and environment, a focus for LKAB has been to reduce the use of fossil fuel as well as to minimize waste and tailings. One of LKABs current environmental initiatives is to investigate the feasibility of recovering and processing apatite from tailings of the LKAB beneficiation process. Further processing of recovered apatite will generate critical raw materials, phosphorous, rare-earth elements, and fluorine. To increase the understanding of the process variability of various analytical parameters in a pilot-scale experiment within this project, both duplicate and replication sampling experiments were conducted during one of the pilot-scale campaigns. The sampling experiments were applied to three separate sampling locations where two different sampling methods were used. Results show that both sampling method and sampling experimental method can affect the results obtained. The case study showed that the sampling variability was higher for sampling locations where grab sampling was applied, in comparison to composite sampling that generated lower sampling variability at one of the sampling locations in the pilot plant. This indicate that the composite sampling method can produce more representative results and should be favourable in future process experiments. The results also indicate that the duplicate sampling experiment is more robust to outliers in comparison to the replication experiment. The duplicate experiment is also able to quantify the process variability and evaluate the relative sampling to process variability which can be an advantage in some cases.

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Introduction

Research and development are vital parts in all industrial companies in the world today. The development and existing and new industrial processes are of utmost importance in order to gain and remain in a business leading position. This is not least the case when it comes to the environmental aspects of industry today where more and more focus is turned to reduce the environmental impact from the processing industries.

Industrial research experiments are conducted in various scales in the mining industry, from laboratory scale to demo-, pilot- and full-scale. The purpose of the experiments can have endless of different purposes, but may include testing of new equipment, testing new additives or reagents as well as testing completely new process systems. Irrelative of the experimental purpose, a mandatory part of the research experiments is often to extract samples and analyse various parameters in order to understand how the process reacts to the process changes under evaluation. Both in full-scale and pilot-scale experiments, the number of sampling locations and the sampling frequency is often increased compared to everyday process sampling. The purpose of this is to maximise conclusion power from the experiment at hand. However, to ensure that the experiment will enable valid conclusions, the understanding and minimisation of sampling variation is crucial. Two effective methods for evaluation of sampling variability in any process sampling situation are the duplicate and replication experiments[1, 2]. This can be applied to any sampling location at any time and will generate an estimation of the sampling variability accompanied by the specific sampling method at the current process state. In order to increase the robustness of the results, the selection of experimental method and design need to be done carefully and repeated experiments may be carried out to cover a larger part of the process variability at hand[3]. The application of sampling experiments in the early phases of a demo- or pilot-scale experiment is an effective way to both understand the total measurement system variability, as well as the possibility to improve the sampling method if the sampling variability I deemed too high to enable representative results to use for experimental evaluation.

LKAB is an iron ore mining company located in the north of Sweden. LKAB has been in operation for over 130 years and its core business is producing highly enriched iron ore products to customers all around the world. LKAB has two underground mines in Kiruna and Malmberget and open pit mines in Svappavaara. Sorting, concentrating, and pelletizing plants are located at all three sites and the final products are shipped from harbours in Luleå and Narvik (Norway). LKAB is positioning its operation as sustainable where the mined magnetite ore only requires a third of the carbon emissions necessary for sintering of pellets compared to hematite ore, or one seventh compared to sintering of fines. LKAB is currently part of several large projects with an aim to reduce the environmental impact from industrial processes. One of these projects include Hybrit, with an aim to produce fossil free steel[4].

Engineers at LKAB conduct experiments in various scales and in all parts of the process value chain with regularity. Process experiments from laboratory- to full-scale are an essential part of the continuous process and product development necessary to ensure that LKAB is able to keep delivering top quality, highly enriched iron ore products to customers worldwide. In the current state of the world, where we are encountering more and more threats to our global climate and environment, a focus for LKAB has been to reduce the use of fossil fuel as well as to minimize waste and tailings.

One of LKABs current environmental initiatives, ReeMAP, is to investigate the feasibility of recovering and processing the apatite from tailings of the LKAB beneficiation process. Further processing of recovered apatite will generate critical raw materials, phosphorous, Rare-Earth Elements (REE), fluorine and gypsum. As LKAB mines iron oxide apatite, the level of phosphorus, suggests that apatite recovery through froth flotation could be a successful method to reduce the tailings from LKAB and at the same time improve the circular economy by utilizing secondary raw material[5]. Mineral processing of low-grade material such as tailings can be very challenging since the feed material characteristics can limit the possibility of high recovery and acceptable grade of the final product. Low grade tailing materials, 2.8-7.2 % P_2O_5 content from LKAB's magnetite beneficiation process have been extensively tested as feed material for apatite recovery by froth flotation in a pilot plant containing all processing steps as a full-scale plant. During initial pilot plant operation, questions regarding which level of variability and changes in experimental data was significant was raised. To be able to answer these questions, the understanding of sampling system variability in relation to process variability is crucial. As a result of these queries, several sampling experiments were included in the following pilot plant trial. To increase the understanding of the process variability of various analytical parameters in the pilot-scale experiments, both duplicate and replication sampling experiments were conducted.

Theory of sampling

Theory of Sampling (TOS) is a complete scientific theory describing both theoretical and practical aspects of how to develop representative sampling processes of particulate material. TOS does for example give complete theoretical definitions of material heterogeneity, as well as correct increment extraction methods and empirical methods for evaluating the variability of sampling systems[6, 7, 8]. Sampling of particulate material is used to enable determination of various parameters for a specific lot of material. However, it is imperative that the complete sampling process is representative, in order to ensure that the analytical results that are obtained from the laboratory sample are both accurate and precise in relation to the lot material that was sampled[9]. With comprehensive knowledge of TOS, representative analytical results can be achieved by applying correct sampling procedures in all parts of the process. Sampling correctness is a fundamental requirement to reach effective process and quality control, as well as to reach valid conclusions from industrial experiments at all scales.

The fundamental sampling principle (FSP) signifies that all particles of the lot material should have equal probability of being collected in the sampling process. This entails that the heterogeneity of the material must be considered, and the sampling process must counteract both the constitutional and distributional heterogeneity, which can be realized by for example composite sampling and correct primary increment extraction from one dimensional material lots. All sampling processes are however coupled with sampling errors that may cause sampling bias and high sampling variability if not respectively eliminated and minimized[8].

Evaluation of sampling variability

There are several statistical and experimental methods for evaluation of the performance of industrial sampling systems and the level of associated sampling errors. In association to industrial research experiments such as pilot plant trials, it is essential to understand the variability contribution from the complete sampling and measurement system in order to decouple this variability from true process variabilities. This may also enable development of more precise sampling systems if variabilities in the initial systems are deemed too high. As pilot plant scale may be the first process trial outside of controlled laboratory studies, new sampling processes are often developed during initial setup and trials. Therefore, experimental evaluation of sampling and measurement variability can be valuable to reach an understanding of how the specific sampling method performs in the specific process location where it is applied.

Two experimental methods that can be applied to any available sampling location are the replication and duplicate experiments. The replication experiment is a fast and effective way of determining the total measurement system variability. The experiment may also be performed in various stages of the measurement system to separate sampling variability from preparation variability and analytical variability[1]. A single replication experiment will give a snapshot of the sampling system variability at the time of the experiment and need to be repeated several times in order to cover larger parts of the process variabilities. The replication experiment is conducted so that the primary increment extraction is repeated ten times, which results in ten separate samples. For further evaluation of the measurement variability, one of these samples can be divided in ten analytical aliquots so that the analytical procedure also is replicated ten times. In this manner, the variability of both primary sampling and measurement can be estimated.

Duplicate experiments entail that a larger process variability can be covered in one single experiment. The duplicate experiment means that every time a primary sample is extracted, this is done in duplicate to produce two separate primary samples extracted in direct repetition. By performing duplication of the primary sampling repeatedly for a specific sample location, the sampling variability can be estimated and put in relation to the process variability. Furthermore, by also duplicating the primary sample and performing duplicate analysis, the measurement variability can be estimated. The complete data set is evaluated with robust analysis of variance (RANOVA) to separate the variability contributions from sampling, analysis (measurement) and between target or process variation[2]. The comparison between the measurement system variability and the process variability is a powerful way of estimating the performance of a measurement system in a specific sampling location. This value is denoted total relative measurement variance in this study, and a general agreement is that this value should not exceed 20% for the sampling and measurement system to be deemed representative[2].

The present case study applied both replication and duplicate experiments during a pilot plant trial with the ReeMAP project at LKAB. The application of both experiments to the same sampling locations enabled evaluation of both the sampling and measurement variability, as well as evaluation of the performance of the two experimental methods in this specific setting. The aim of the sampling experiments was to understand the magnitude of the sampling and measurement variability in order to enable valid conclusions regarding true process variability during the pilot plant trial. Furthermore, by applying both experimental methods to the same sampling locations, the results from both methods can be compared to possibly determine which method is the most applicable in future pilot plant trials within LKAB.

ReeMAP

Metallurgical test work for the project studying apatite recovery from fresh tailings started at bench scale since it was more resource efficient, and screening tests could be carried out in a more efficient way. Results from the metallurgical bench scale test work were positive and indicated that apatite recovery from fresh tailings would be feasible[10]. Continuous froth flotation test work at bench scale is difficult to carry out and it is therefore beneficial to carry out continuous pilot scale test work with circulating loads. A mobile froth flotation pilot plant was designed and acquired from a mineral processing equipment supplier. Apart from technical requirements, the possibility of correct sampling of all, or at least as many as possible, of the process streams in the pilot was an important aspect during the designing phase of the pilot. This is considered as crucial since representative sampling is a key parameter to be able to draw valid conclusions from the test work results and thereby make the correct decisions regarding which of tested flowsheet designs are the most advantageous.

The pilot for the flotation test work consists of two separate 20 feet long containers, with mineral processing equipment installed. The first container in the pilot set up, container A, is for preparing of the mineral slurry for froth flotation and has screening equipment, wet low intensity magnetic separation, hydrocyclones, stirred storage tanks and one flotation cell. The second container, container B, is solely dedicated to flotation and consists of a flotation blower for providing the flotation air and seven individual flotation cells. Most of the sampling locations for the process streams are in connection with vertical tank pumps used for transporting the slurry between different unit operations in the process flowsheet, taking full advantage of TOS' 1-D lot transformation principle.

The first step in the pilot plant is removal of +355 µm particles by wet screening. After screening, maximum particle size that needs to be considered when choosing sampling equipment is therefore 355 µm. Slurry streams from the flotation cells are flowing by gravity into the tank of the pump and the sample was taken from that laminar flow, Figure 1.

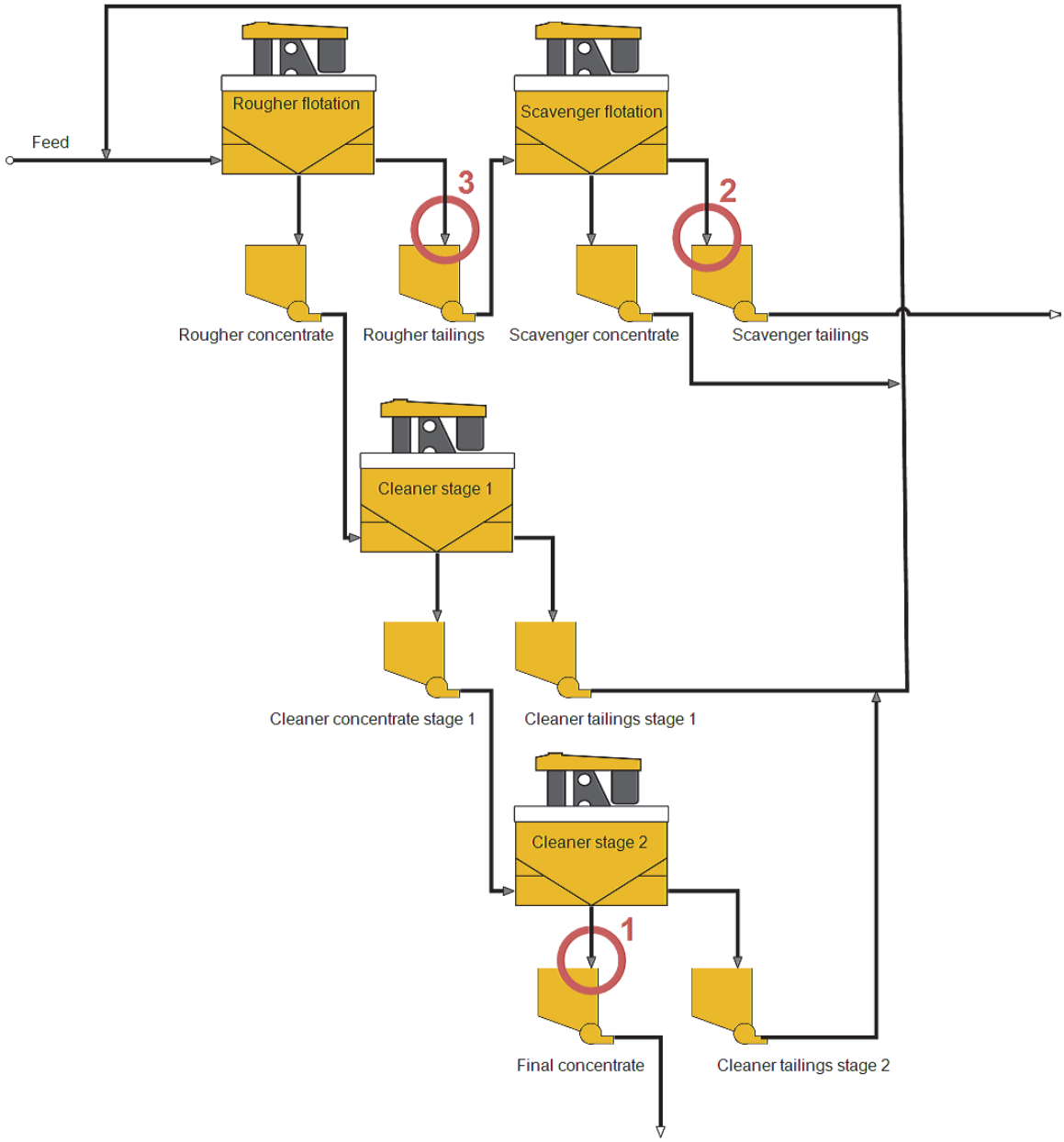

Figure 1. Simplified process flow sheet for the flotation pilot plant. Evaluated sampling locations indicated by #1: Final Concentrate, #2: Scavanger Tailings, #3: Rougher Tailings.

Key parameters to study and evaluate during the pilot scale test work were process stability, process behaviour for different flotation collectors and effects when feed composition of the mineral slurry varied. The sampling points evaluated in this case study were those that generate the most important process data that imply the necessity for changes in comparison to the other sampling points. These process streams are Rougher Tailings, Scavenger Tailings, Final Concentrate, Figure 1.

Analysis results from the Rougher and Scavenger tailings had shown inconsistency (see further below) in the test campaign prior the one described in this paper. The assay for these two tailings streams holds importance about the status of the flotation process and if it is necessary to adjust the amount of added collector, since collector is added to the rougher and scavenger and if changes in collector amount or allocation between the two flotation cells should be implemented. The apatite recovery will be reduced if not enough collector is added and if too much collector is added the quality for the Final Concentrate will be lowered. Satisfactory sampling of the final product of a process is always important and this was the reason for choosing Final Concentrate as the third sampling point to investigate. Noticeable for the three process streams evaluated in this case study is the large difference in flow between the three sampling locations, where the two tailing slurry streams have a higher flow than the Final concentrate (froth product), Table 1.

Table 1. Mean values for the weight %-solids and slurry flow for the three sampling points evaluated in the case study.

	Rougher tailings	Scavenger tailings	Final concentrate
Weight %-solids (%)	26.1 – 31.6 (mean: 29.1)	28.3 – 33.4 (mean: 30.7)	19.8 – 31.7 (mean: 27.0)
Slurry flow (dm^3/h)	955	855	108.3
Slurry flow (dm^3/min)	15.9	14.3	1.8

Case study - Sampling experiments at the ReeMAP plant trials

The sampling experiments in this case study were conducted during one of the first fully functional pilot plant trials conducted within the ReeMAP project. The sampling experiments were applied to three different sampling locations, Rougher Tailings, Scavanger Tailings and Final Concentrate, Figure 1, where two different primary sampling methods were used. The selection of sampling locations was based on results from the first pilot plant trial, where inconsistencies in the analytical result from Rougher and Scavanger Tailings indicated that there might be an adverse effect from sampling variability. Thus, reducing the possibilities to draw valid conclusion from the process in regard to the amount of added collector as well as related to process variabilities and output. Rougher and Scavanger Tailings are sampling locations with slurry flows of around 15 dm^3/min. The larger flow for the tailings is due to the limited amount of apatite and most of the flotation process feed material will report to the tailings. The Final Concentrate is the froth product from flotation, with a flow of around 1,8 dm^3/min at sampling location, Table 1. Both duplicate and replication sampling experiments were applied to all three sampling locations to enable evaluation of the two different experimental approaches as well as the sampling system variability.

Primary increments from Scavanger Tailings and Final Concentrate were extracted by allowing the entire process stream from the outlet tube fill a container, until enough material for analysis was collected, Figure 2. Rougher Tailings on the other hand was sampled by taking four increments with a manual sample cutter, Figure 2. Eight duplicate sampling rounds individual sampling rounds were conducted on each of the sampling location, where was applied in each round and a complete replication experiment was performed twice, Table 2. The sampling rounds were spread out during plant trial operation so that each experimental round was conducted during time periods with stable process parameters.

The collected material from each sampling location was dried at 105 ºC for 24 hours and then divided into analytical aliquots using a riffle splitter. Roughly 100 g was prepared for the chemical laboratory and pulverized using a Herzog HP-MA pulverizing mill to less than 100 µm. From the 100 g pulverized sample, 0,72 g was extracted by taking several increments using a spatula and mixed with 8,00 g lithium tetraborate as flux, along with one drop of 20 wt % lithium bromide as non-wetting agent. A fusion borate disc was prepared using an electrical furnace. The prepared borate disk was analysed for chemical composition using a simultaneous WDXRF.

Figure 2. Left: Container used to collect material from the Scavanger Tailings and Final Concentrate sampling locations. Right: Manual sample cutter used for sampling Rougher Tailings, with a cutting aperture of 18 mm.

Table 2. Sampling schedule for the duplicate method and replication experiment. The duplicate sampling experiment was conducted on every sampling round, while the replication experiment was conducted in two of the sampling rounds.

	Duplicate sampling experiment	**Replication sampling experiment**
Sampling day 1	Two duplicate sampling rounds Two XRF- analyses per sample	
Sampling day 2	One duplicate sampling round Two XRF- analyses per sample	One replication experiment with 10 primary samples 10 replication XRF-analyses on one of the primary samples
Sampling day 3	Two duplicate sampling rounds Two XRF- analyses per sample	
Sampling day 4	Two duplicate sampling rounds Two XRF- analyses per sample	
Sampling day 5	One duplicate sampling round Two XRF- analyses per sample	One replication experiment with 10 primary samples 10 replication XRF-analyses on one of the primary samples

The duplicate sampling experiment was conducted with a balanced empirical design for application of RANOVA. This enables separate estimations for the sampling variability, the analytical variability as well as the process (between-target) variability for each sampling location, Figure 3. The duplicate sampling experiment was done by extracting eight duplicate primary samples in a period of 5 days during the full pilot plant trial. The duplicates where randomly distributed during the plant trial but at each time making sure that the operating conditions of the plant was stable and not affected by any noticeable adverse effects. XRF-analysis was performed on each duplicate analytical sample, 1:1A, 1:1B, 1:2A, 1:2B, etc, Figure 3.

The replication sampling experiment was conducted twice, on two random days during the plant trial. Ten primary samples were collected in rapid succession from each sampling location (1.1-1.10). Thus, the replication experiments will only provide two 'snap-shots' of the total variability (sampling + subsampling + preparation + analysis) for the two time periods, Table 2. Each of the ten primary samples was analysed with XRF for chemical composition, allowing estimation of the measurement variability (sampling and analytical variability). One of the ten primary samples were further split into ten sub-samples and each of these analytical aliquots were analysed with XRF, allowing for the analytical repeatability to be estimated separately, Figure 4.

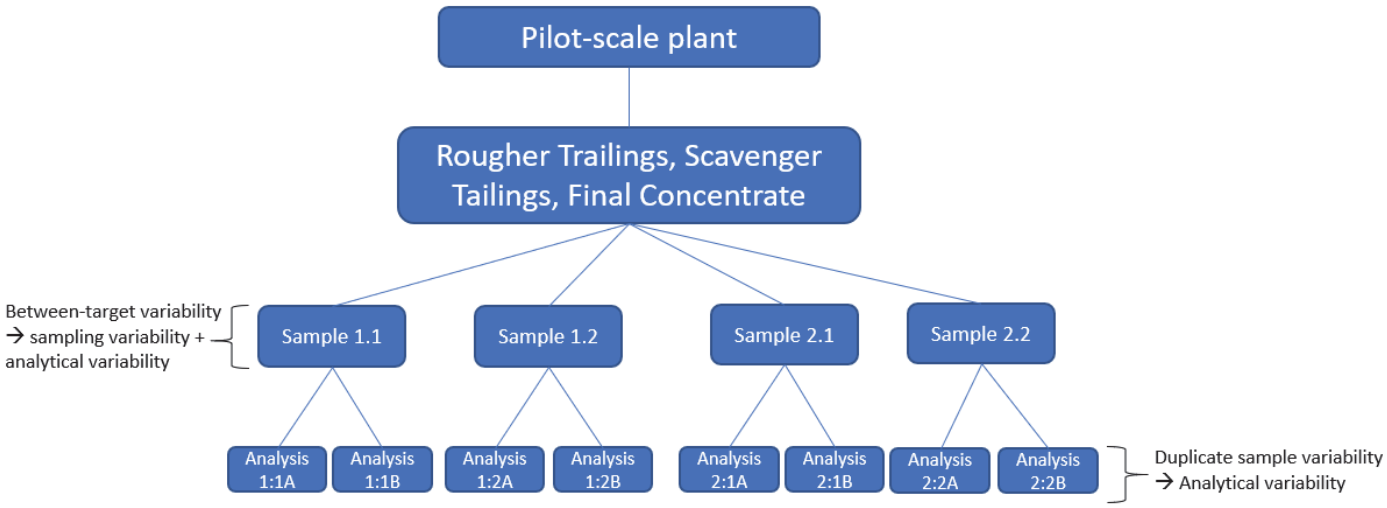

Figure 3. Design for the balanced empirical duplicate sampling experiment. RANOVA was used to separate the variability contributions from sampling, analysis (measurement) and between target or process variation.

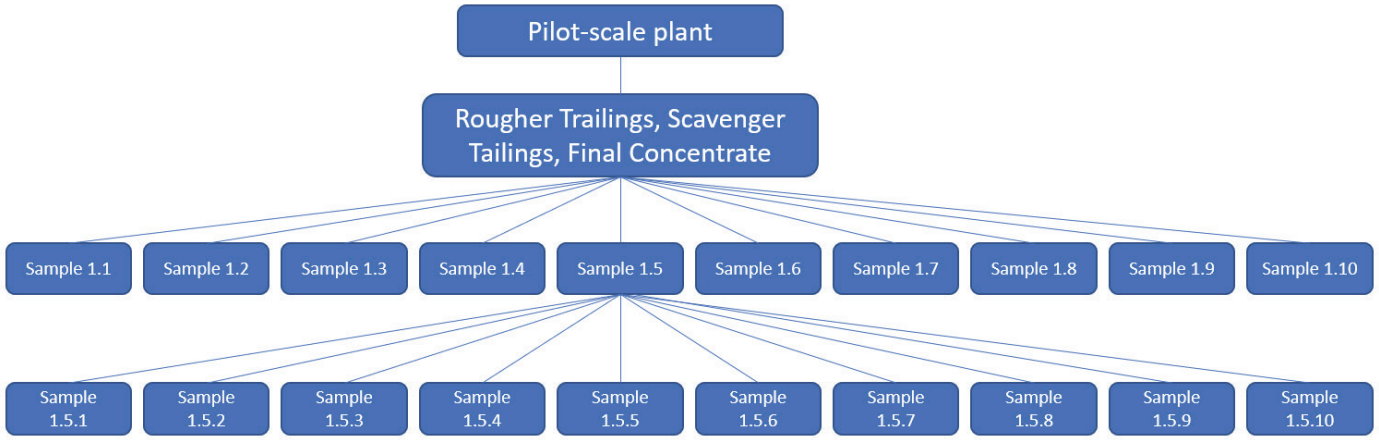

Figure 4. Design for the replication sampling experiment.

Results

The results from the duplicate sampling experiments were analysed using RANOVA and the expanded relative uncertainties (U) could thereby be divided into variabilities stemming from analysis ($U_{a\text{-duplicate}}$), sampling ($U_{sampling\text{-duplicate}}$) and sampling + analysis ($U_{measurement\text{-duplicate}}$), Table 3. The expanded uncertainties in this case study have been calculated with a coverage factor of K = 2, which corresponds to a 95% confidence interval. In order to understand the relation between measurement system variability (sampling + analysis) and process (between target) variability, the total relative measurement variance and mean value during the experiment have been calculated for each chemical parameter, Table 3. The uncertainties from the duplicate sampling experiment have been calculated for all eight duplicates together, meaning that the between target uncertainty corresponds to the process variability of the pilot plant.

The results from the replication experiment were used to calculate the expanded relative uncertainties (U) stemming from analysis ($U_{a\text{-replication}}$), sampling ($U_{sampling\text{-replication}}$) and sampling + analysis ($U_{measurement\text{-replication}}$) which were estimated by calculating the mean value and standard deviation for the replicated samples, as well as the ten sub samples. U is expressed as the Coefficient of Variation (COV) with a coverage factor of two, Table 4. The relative total measurement variance expressed as the COV and the mean value during the experiment for each chemical parameter have also been calculated, Table 4 and 5.

Table 3. Summary of expanded relative uncertainty from the sampling locations Rougher Tailings, Scavenger Tailings, Final Concentration during the duplicate sampling experiment. The uncertainty is estimated from RANOVA of duplicates. Coverage factor = 2, which describes a 95% confidence interval for the mean value.

Chemical parameter	Expanded relative uncertainty from analysis			Expanded relative uncertainty from sampling			Expanded relative uncertainty from measurement (sampling + analysis)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	1,3%	3,9%	4,9%	5,5%	20,9%	37,7%	5,6%	21,3%	38,0%
P	2,8%	10,0%	0,9%	6,9%	6,0%	1,4%	7,4%	11,7%	1,7%
SiO2	0,7%	1,3%	6,7%	1,1%	4,3%	17,2%	1,4%	4,5%	18,5%
Al2O3	1,1%	1,9%	14,7%	1,9%	5,3%	19,2%	2,2%	5,6%	24,2%
CaO	1,5%	1,8%	0,9%	2,6%	5,2%	0,6%	3,0%	5,5%	1,1%
MgO	0,8%	1,6%	19,4%	1,5%	4,8%	52,5%	1,8%	5,1%	56,0%

	Total relative measurement variance			Relative "Between-target" variance			Mean value		
Chemical parameter	% of total variance for measurement (sampling + analysis)			% of total variance for "Between-target"			Mean value/concentration during experiment (%)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	24,0%	99,3%	24,3%	75,98%	0,7%	75,7%	9,10	11,77	0,43
P	1,5%	1,0%	5,0%	98,51%	99,0%	95,1%	0,88	0,22	16,69
SiO2	6,2%	94,4%	2,6%	93,85%	5,7%	97,4%	48,83	48,90	1,03
Al2O3	9,3%	100,0%	6,2%	90,74%	0,0%	93,8%	9,79	9,77	0,10
CaO	2,1%	19,1%	13,5%	97,95%	80,9%	86,5%	8,46	6,25	54,17
MgO	4,3%	24,4%	8,8%	95,66%	75,6%	91,2%	8,28	8,27	0,18

Table 4. Summary of relative uncertainty from the sampling locations Rougher Tailings, Scavenger Tailings, Final Concentration during the first replication sampling experiment. The expanded uncertainty is estimated from replication experiment and expressed as the COV with a coverage factor of 2.

Experiment 1	$U_{a\text{-replicate}}$			$U_{sampling\text{-replicate}}$			$U_{measurement\text{-replicate}}$		
Chemical parameter	Expanded relative uncertainty from analysis			Expanded relative uncertainty from sampling			Expanded relative uncertainty from measurement (sampling + analysis)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	3,4%	1,6%	1,9%	2,4%	18,4%	25,0%	2,7%	18,5%	25,0%
P	5,5%	3,6%	0,6%	24,6%	7,8%	3,1%	25,1%	8,7%	3,1%
SiO2	0,5%	0,5%	2,8%	1,3%	3,7%	31,7%	1,4%	3,8%	31,8%
Al2O3	1,7%	0,6%	13,8%	0,5%	3,7%	23,2%	1,6%	3,8%	25,8%
CaO	2,0%	0,7%	0,7%	5,8%	3,6%	1,4%	6,1%	3,7%	1,5%
MgO	1,7%	0,6%	5,2%	1,1%	3,3%	48,3%	2,1%	3,3%	48,4%

Experiment 1	Relative variance			Mean value		
Chemical parameter	Variance for measurement (sampling + analysis)			Mean value/concentration during experiment (%)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	1,4%	9,2%	12,5%	8,90	10,25	0,61
P	12,5%	4,3%	1,6%	0,63	0,074	15,80
SiO2	0,7%	1,9%	15,9%	49,53	50,70	1,85
Al2O3	0,8%	1,9%	12,9%	10,53	10,74	0,18
CaO	3,0%	1,9%	0,8%	7,62	5,70	53,33
MgO	1,0%	1,7%	24,2%	8,27	8,23	0,51

Table 5. Summary of relative uncertainty from the sampling locations Rougher Tailings, Scavenger Tailings, Final Concentration during the second replication sampling experiment. The expanded uncertainty is estimated from replication experiment and expressed as the COV with a coverage factor of 2.

Experiment 2	$U_{a\text{-replicate}}$			$U_{sampling\text{-replicate}}$			$U_{measurement\text{-replicate}}$		
Chemical parameter	Expanded relative uncertainty from analysis			Expanded relative uncertainty from sampling			Expanded relative uncertainty from measurement (sampling + analysis)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	2,2%	3,3%	2,5%	15,1%	49,1%	27,7%	15,2%	49,2%	27,8%
P	3,3%	9,5%	0,5%	25,1%	16,5%	0,9%	25,3%	19,3%	1,1%
SiO2	0,8%	0,7%	4,3%	3,4%	9,7%	9,4%	3,5%	9,7%	10,2%
Al2O3	1,4%	1,8%	36,9%	6,9%	9,9%	34,7%	7,1%	10,1%	15,5%
CaO	1,4%	3,0%	0,6%	8,0%	7,5%	0,5%	8,1%	8,1%	0,8%
MgO	1,2%	1,2%	2,5%	3,6%	9,2%	17,7%	3,8%	9,3%	17,8%

Experiment 2	Relative variance			Mean value		
Chemical parameter	Variance for measurement (sampling + analysis)			Mean value/concentration during experiment (%)		
	Rougher Tailings	Scavenger Tailings	Final Conc.	Rougher Tailings	Scavenger Tailings	Final Conc.
Fe	7,6%	24,6%	13,9%	9,93	10,38	0,53
P	12,7%	9,7%	0,5%	0,74	0,31	16,18
SiO2	1,8%	4,8%	5,1%	48,47	49,85	1,89
Al2O3	3,5%	5,0%	7,7%	9,86	10,06	0,15
CaO	4,0%	4,1%	0,4%	7,66	6,40	53,42
MgO	1,9%	4,6%	8,9%	8,44	8,55	0,49

Discussion

The results from this case study clearly show that the sampling system largely affects the level of total measurement system variability. Especially when comparing the sampling variability between Rougher Tailings and Scavenger Tailings, where different primary sampling methods were applied, while the mean concentration of most parameters are similar. The estimated sampling variabilities for Rougher Tailings and Scavenger Tailings are significantly different for several parameters, where Rougher Tailings have a smaller sampling variability compared to Scavanger Tailings. This strongly indicates that the primary sampling method used for Rougher Tailings, where four increments were collected with a manual sample cutter, results in lower sampling variability than collecting the complete process stream in one larger container. Collecting a sample with this single round container means that the primary sample extraction violates several of the main principles of the TOS and leads to increment delimitation and extraction error among many others. This also imply that only one increment is collected for each sample, and this is extracted in an incorrect manner, i.e. a grab sample that can never be representative. The case study results thereby imply that composite sampling, where several increments are collected and combined to a primary sample, results in lower variability than collecting a single large grab sample. This conclusion is supported by the Theory of Sampling, where composite sampling is strongly recommended in order to achieve representative samples.

The relative sampling uncertainty for Final Concentrate is higher compared to Rougher Tailings, but the mean value for the chemical parameters for Final Concentrate also differs compared to Rougher Tailings and Scavenger Tailings. This complicates the comparison as relative uncertainties always correlates to the concentration level of the chemical parameter at hand. In addition to the differences in mean values, the physical character of the material also differs, where the Final Concentrate is a froth product from the froth flotation process, while Rougher Tailings and Scavenger Tailings are liquid slurry tailings from the same process.

The duplicate sampling experiment was conducted eight times during a five-day period, allowing for estimation of the process variation. An important advantage from the duplicate sampling experiment, is that the different variabilities are estimated over a larger concentration interval, due to the inclusion of the process variability over a longer time-period compared to the replication experiment. The duplicate experiment also gives the possibility to compare the variability in the measurement system to the total process variability, which gives an indication of the ability of the measurement system to describe the true process fluctuations. This 'total relative measurement variance' is calculated as the variance for sampling + analysis divided by the between target variance (process variability) and is a valuable indication of how well the measurement system is able to describe the process variability. The total relative measurement variance for Rougher Tailings and Final Concentrate are both below 20 % for most of the chemical parameters, while close to 100 % for most of the chemical parameters for Scavenger tailings. This implies a difficulty to evaluate process data from Scavenger tailings as it is impossible to know if the variability in the data comes from actual process changes or solely from the measurement system. Sampling and measurement system variabilities of this magnitude makes it impossible to draw valid conclusions from an industrial experiment such as this pilot-plant campaign[11].

The relative analytical uncertainty estimated from both the duplicate experiment and the replicate experiment is larger for the Final Concentrate, compared to the two sampled tailings, for most of the chemical parameters. Noticeable is that the Final concentrate is a froth product that may be more affected by the inter-laboratory sample preparation variability (which in this study is included in the analytical variability). This could indicate that the in-laboratory sample preparation and analytical method is more suitable for the two tailings products containing higher concentrations of iron and silica, in comparison to the froth product of Final concentrate with high concentration of phosphorus and calcium. This is likely do to the fact that the in-house laboratories used in this case study are more adapted for the routine iron ore samples from the concentrating and pelletising plants of LKAB.

The results from both the duplicate- and replication sampling experiments showed that the two experimental methods estimate similar analytical and sampling variabilities in the current case study. However, the variabilities observed in the two separate replication experiments showed diverse results for some chemical parameters. This is due to the fact that one of the ten primary samples in the second replication experiment is a significant outlier compared to the rest of the data, and therefore greatly affect the estimated sampling variability.

The replication experiment was only conducted twice in this case study and is therefore more sensitive to outliers. An example of this is replication sample 2.6 from Scavenger Tailings, table 6. To ensure that this was not an analytical error, new analyses was conducted on the archived material from both the laboratory as well as from the sampling experiment. Both additional analyses showed the same outlying result. One reason for this could be beneficiation of hematite in the tailing product of the froth flotation process, which can suddenly release into the sample stream and result in such an outlying value. As the root cause for this outlier has not been possible to determine, the authors deem that repeating the calculation after removal of the outlier would most likely underestimate the sampling variability and is therefore not a feasible alternative. This one outlier is the reason for the estimated sampling variability to be higher for the second replication experiment compared to the first one. This shows the strength of duplicate sampling experiments in combination with RANOVA as a suitable method to handle scenarios with possible outliers. This also indicate that it is of great value to perform replications experiments regularly to monitor the sampling variability over time and reduce the effect of isolated outliers to the overall estimation of sampling variability.

The results from the replication experiments shows that this method is sensitive for single outliers. To ensure the validity of replication sampling experiments, it is therefore important to reproduce the experiment several times in order to understand the sampling process fully, as well as to enable identification of single outliers and how they may affect the sampling process. Furthermore, in a process where these kinds of large and sudden process variations do occur, the sampling process must be designed to handle the process variations so that necessary changes are detected, while sudden incidents that do not affect the overall process performance does not corrupt the data analysis, and therefore affect the conclusion power for the process experiments. However, the replication experiment is a rewarding method to reach quick conclusion regarding the variability of the applied primary sampling methods. The replication experiment in this case study indicates that composite sampling with several increments is less likely to result in outliers and thereby more robust for valid conclusions regarding process changes.

Table 6. XRF-analysis data on each of the ten primary replication samples, from the two separated experiments conducted on the Scavanger Tailings. Primary sample 2.6 show deviating XRF-results compared to all the other samples in both replication experiments. This outlier strongly affects the sampling variability estimation for the replication experiment.

Scavenger Tailing	Replication sample	Fe (%)	P (%)	SiO2 (%)	Al2O3 (%)	CaO (%)	MgO (%)
Experiment 1	1.1	9,998	0,073	50,580	10,788	5,671	8,283
	1.2	9,460	0,069	51,209	10,879	5,702	8,302
	1.3	10,284	0,075	50,672	10,781	5,699	8,260
	1.4	9,960	0,076	51,022	10,847	5,744	8,328
	1.5	10,075	0,076	50,715	10,756	5,722	8,265
	1.6	12,668	0,075	48,256	10,252	5,423	7,904
	1.7	9,246	0,076	51,771	10,982	5,728	8,353
	1.8	9,972	0,079	51,288	10,779	5,834	8,273
	1.9	10,770	0,071	50,316	10,554	5,743	8,074
	1.10	10,022	0,070	51,189	10,809	5,695	8,210
Experiment 2	2.1	11,137	0,296	49,214	9,929	6,299	8,410
	2.2	10,858	0,385	49,063	9,897	6,587	8,483
	2.3	9,360	0,311	50,779	10,251	6,461	8,660
	2.4	10,344	0,270	50,030	10,293	6,163	8,657
	2.5	9,366	0,329	50,851	10,162	6,582	8,731
	2.6	17,183	0,295	43,433	8,719	5,772	7,490
	2.7	8,645	0,306	51,324	10,421	6,472	8,797
	2.8	8,923	0,301	51,502	10,412	6,481	8,802
	2.9	9,518	0,321	50,812	10,161	6,584	8,690
	2.10	8,480	0,321	51,485	10,390	6,569	8,797

Conclusions

This case study shows that the estimated sampling variability is largely affected by the applied primary sampling method together with the design of the sampling experiment. The total relative measurement variance from the duplicate experiment was under 20 % for most of the chemical parameters for Rougher Tailings and Final Concentrate. This is considered acceptable since no predetermined requirement was set for any of the sampling locations. The total relative measurement variance for Scavenger Tailings was over 20 % for most of the analysed chemical parameters, and the sampling variability was contributing to the largest part of the measurement system variance. This is a clear indication that the primary sampling method has a large influence on the total measurement system variability within this case study. It also highlights the importance of adapting and evaluating the sampling methods individually for each sampling location and in all industrial experiment setups.

The duplicate experiment in combination with a RANOVA, was shown to be a more comprehensive method to estimate the measurement variabilities in industrial experiments, compared to the replication experiment. An important benefit with the duplicate sampling experiment is the generation of less samples to handle for sampling- and laboratory staff, especially considering a full-scale sampling experiment replicating both sampling, sometimes sample preparation, and analysis. Duplicate sampling experiments also have the advantage of covering a wider timeframe and enable evaluation of the total process variability. This allows for comparison between measurement system and process variability which clearly indicate the possibilities to draw valid conclusions from the measurement data produced.

The sampling variability in the evaluated pilot plant trial was lower for the composite sampling process using a manual sample cutter to collect several increments for each primary sample for Rougher Tailings. The sampling process using a sample container to collect one grab sample from the process stream, applied on Scavenger Tailings, resulted in larger sampling variability. The composite sampling process should therefore be advocated for use on all sampling locations in future pilot plant trials. Comparison between the sampling variability for Final Concentrate to the two tailings products is challenging as the mean value for all parameters differ a lot, together with this being a froth product compared to the tailings being slurries. These two facts also resulted in discrepancies in analytical uncertainty between these two material types.

The results from this case study show that sampling experiments are valuable in order to estimate the variability stemming from both sampling and analysis for different sample locations and various materials being sampled. By applying sampling experiments in initial pilot plant trials, as well as other industrial experiments at various scales, the complete measurement process can be evaluated, and primary sampling methods can be improved to reach lower sampling variability in future plant trials. The application of sampling experiments in this case study could clearly show that the composite sampling method resulted in significantly lower sampling variability than the grab sampling method. This is an important knowledge in further pilot plant trials where the composite sampling method can be applied to all sampling locations in order to reduce the measurement system variability. The replication experiment is concluded to be an efficient method to receive a snapshot of the performance of the complete sampling and measurement system in any industrial process sampling situation. An important advantage with the replication experiment is that it is a fast and effective way to give an indication of the level of sampling variability connected with the primary sample extraction method. However, in order to also understand the correlation between the total measurement system variability and the process variability, the duplicate sampling experiment is a rewarding method. This understanding may for example be important in order to evaluate if a small change in process data actually is of importance or if it may be explained by sampling and measurement variability.

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