

HETEROGENEITY PROFILING: A TECHNIQUE TO IMPROVE GEOCHEMICAL SAMPLING AND ANALYSIS FOR AMD ASSESSMENTS

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ABSTRACT

Heterogeneity is the measure of the degree of compositional variability of a material. For typical waste geochemistry assessments heterogeneity affects range from macroscale (inter-sample) to microscale (intra-sample) heterogeneity. Or, put another way, heterogeneity effects are scalar as well as spatial in nature. In the majority of cases therefore, the degree to which the scalar effects of heterogeneity are understood is likely to be a key factor in determining how successful a characterisation program is likely to be.

As part of routine geochemical characterisation programs, materials are generally classified based on the analysis of a finite (often small) number of samples. Although these effects of heterogeneity are acknowledged it is not common for detailed assessment of heterogeneity to be routinely carried out as part of acid mine drainage (AMD) assessments.

As part of a large scale materials assessment programme, O'kane Consultants (OKC) has taken the opportunity to study the effects of material heterogeneity on geochemical assessment in detail. As part of the assessment, OKC has developed and trialled a profiling tool to allow the quantitative assessment of the scalar and temporal effects of heterogeneity on geochemical classification. The tool has been developed and used to gain an understanding of the following

- *The influence of intra-sample particle size*
- *The influence of inter- and intra-sample compositing*
- *The influence of intra-sample mineralogy*
- *The influence of sample preparation (crushing, grinding, sieving, splitting)*

1.0 INTRODUCTION

The geochemical characterisation of materials forms the fundamental basis of acid and metalliferous drainage (AMD) studies. Because of the need for a scientific and rational approach to materials characterisation, internationally accepted testing standards (e.g. ASTM), and guideline documents have been developed to cover the sampling and characterisation process. These documents have been developed by technical experts and specialist groups (e.g. INAP) and, are generally used as standard reference documents throughout the industry. The vast majority of these documents cover the topic of sampling accuracy, precision and correctness and most have a strong focus on the fundamental principles of analytical precision given in the context of laboratory analysis. Much of the focus is given to analytical precision and measurements of this concept. However, when dealing with the kind of heterogeneous materials encountered during AMD studies, the term analytical precision must clearly be distinguished from attempts to determine sampling accuracy and, indeed, sampling error in relation to materials characterisation. Previous studies and decades of research within the resources industry have highlighted that sampling

errors relating to insufficient sampling frequency and sampling methodology, rather than analytical precision, are in many cases the controlling factor on data quality. The discussion of how to improve data quality and therefore how to best characterise the heterogeneous material should therefore move away from the current central focus of analytical precision to be re-focused on how to improve sampling method and frequency as the most effective means to address what and how materials are sampled and characterised.

It is interesting to note that much of the technical developments of sampling theory and practice has been developed by the mining industry over many years. The establishment of Joint Ore Reserves Committee (JORC) 2012 reporting standards for example are a case in point as they have very comprehensive guidelines with respect to reporting of sampling methods, measurements of sampling error and correctness. Because AMD assessments are typically carried by environmental geoscientists and not resource geologists, these theories, methods and practices developed by the mining industry have not generally been integrated into AMD assessments.

The lack of integration of the “theory of sampling” (TOS) used by the mining industry into AMD studies, a number of problems are commonly and repeatedly raised during AMD assessments for which solutions have not been consistently developed or adopted.. A selection of these questions include:

- What size should the samples be?
- What preparation method should be carried out prior to analysis?
- How much analysis is required?
- How should data quality objectives (DQO)s be defined and assessed?

Many published AMD related guidance documents offer little in the way of specific guidance on how to tackle some of these questions.

This paper has been prepared in an attempt to integrate some of the principles of TOS and practice from the resource characterisation industry to AMD studies, and to provide a useful tool for answering the questions given above.

2.0 SAMPLING THEORY

A comprehensive publication of the theory of sampling of particulate materials was published in 1979 by Dr Pierre Gy, the last publication being 1993 by means of a translated overview of his work by Francis F. Pitard (Pitard 1993). The theory covers all facets of sampling, how errors are generated, how errors can be reduced or eliminated, and how the residual error can be estimated. The theory of sampling (TOS) has been widely adopted in the resources industry.. In contrast, it is not common for TOS to be familiar to many in the environmental geoscience field which includes many practitioners of AMD management. Indeed to the authors’ knowledge, TOS is not routinely covered in university courses such as environmental science, and it is very uncommon to see AMD-based research papers produced that make reference to TOS.

TOS indicates that total sampling variance is the preferred measure of the total sampling error, but determining the variance into its component parts is very challenging. Ten sources of sampling error (Pitard, 1993) that contribute to non-representativeness of samples have been identified and include:

1. In situ Nugget Effect (NE)
2. Fundamental sampling error (FE)
3. Grouping and segregation error (GE)
4. Long-range heterogeneity (quality) fluctuation error (QE1)

5. Long-range periodic heterogeneity (quality) fluctuation error (QE2)
6. Increment delimitation error (DE)
7. Incremental extraction error (EE)
8. Weighing error (WE)
9. Preparation error (PE)
10. Analytical error (AE)

Errors 1-5 are random and are related to the intrinsic properties (heterogeneity) of the materials we are analysing, errors 6-10 relate to laboratory analytical techniques.

Consideration of all ten of these errors is far beyond the scope of this paper, and in some cases is not relevant to many AMD sampling programs, however for many waste material characterisation assessments, it is FE that is of primary importance. Given this fact a large proportion of the paper is given to the concept of FE.

Through numerical calculation and testing programs, it is possible to estimate, measure and influence FE by determination of a materials heterogeneity and interrogation/optimisation of the sampling process used as part of analysis.

It is relevant to note that FE is the only error that can be reasonably estimated before sampling is carried out (Minnitt et al 2007).

As previously stated, industry standard AMD publications tend to focus on AE as the key measure of sampling representativeness as this is one of the most widely quoted means of assessing sampling accuracy. As can be seen, this is only one of the ten possible errors however and with modern equipment AE is commonly of much less importance than FE. Analytical errors for modern equipment can be expected to be less than 5% in many instances based on quoted values by commercial laboratories for standard analysis like ICP (metals). Errors related to FE however have been found to be >40% in many case studies.

It is relevant to note that AE values of >5% are in fact commonly reported in many material characterisation studies so the reader may question the 'discounting' of AE as part of this assessment but, upon even a cursory review of how laboratories/consultants/industry report AE, it likely that it is FE that is being incorrectly reported as AE. This 'accusation' can be proven simply by looking at commercial laboratory reports that quote QA/QC data that quantify AE but make no attempt to quantify FE.

Generally, the error introduced by modern laboratory-based analytical instrumentation as analytical bias is likely to be relatively low; therefore the precision of laboratory analytical test data is high. A study carried out in Europe (CLAIRE, March 2004) indicates that for a given case study the effects of sample heterogeneity on sampling method (FE) was by far the greatest cause of uncertainty rather than analytical bias (AE). Precision bias was estimated at $\pm 83\%$ of the concentration value for the sampling method (due to effects of heterogeneity), but was much lower at $\pm 7.5\%$ for analytical method. The overall random component of uncertainty (FE) was estimated as being $\pm 83.6\%$. The majority of the overall variability was therefore related to the effects of intra sample heterogeneity on sampling (FE) method rather than analytical factors (AE).

From a practical point of view the principles of TOS would indicate that the standard approach to estimating AE by undertaking laboratory duplicate sampling is a process that unless done with care is at the mercy of FE effects.

To understand FE, heterogeneity must first be understood and defined.

3.0 HETEROGENEITY

Heterogeneity is the measure of the degree of compositional variability of a material and is a scalar concept (i.e. it is evident over micro- to macro-scales). For the purposes of a waste materials assessment, two broad scales can be considered over which heterogeneity will operate:

1. Inter-sample (macro-scale)
2. Intra-sample (micro-scale) heterogeneity.

Inter-sample heterogeneity: This defines large scale variability differences between sample locations, i.e. the variability in composition between 2 samples taken at different spatial locations m to 100m apart. For example, mineralisation may be concentrated within a particular material (e.g. in a vein of primary sulfide mineralisation), at a particular location (near a fault zone), or at a particular depth (possibly a layer of material in a waste dump). The degree of inter-sample heterogeneity will therefore have a potentially significant impact on the ability of the sampling programme to characterise the geochemistry of the material on site.

Intra-sample heterogeneity: This defines small scale heterogeneity of a material with respect to the differences in geochemical composition within a 2kg RC sample for example. At these smaller scales, various mineral phases may be present and unequally distributed (e.g. isolated macro pyrite crystals, variable surface crusts of secondary minerals), and various sources of material may be present (e.g. overburden, ore, varying grade of alteration minerals).

The importance of determining between inter- and intra-sample variability effects cannot be overstated when it comes to interpretation of sampling data for AMD assessments. Spatial trends for example are entirely dependent on the determination of inter-sample variability. However if the intra-sample variability has not been well established prior to analysing inter-sample variations, then the data points used for the spatial analysis and variographic analysis may be not be considered representative.

Because advances in variography are beyond the scope of this paper, inter-sample variability will not be considered further. It is intra-sample heterogeneity that will instead be the focus of discussion.

4.0 DETERMINATION OF HETEROGENEITY

Each type of material has specific characteristics in regard to the manner in which the mineral of interest is distributed in the host rock.

Two major characteristics of heterogeneity were identified by Gy (1982):

- Compositional heterogeneity (CH): difference in composition between individual fragments of a sample due to the inherent natural compositional variability. The greater the difference in composition between each fragment, the greater the compositional heterogeneity
- Distribution heterogeneity (DH): difference in average composition of the lot (sample) from one place to another. This is reflected in irregular distribution in grade in groups of fragments. Distribution heterogeneity can be influenced by particle density and size.

It should be noted that the term 'fragment' for the purpose of geochemical sampling assessments can include a single fragment (single gravel fragment) but it can also include groups of very small material fragments of the same weight. For example a 1kg lot split into

50 separate but equal 20g pulp samples is given to comprise 50 fragments of the lot for the purposes of assessment.

Factors that influence CH include size, shape, density, mineralogical composition of fragments within a sample. Because these factors are inherent to geological materials it is apparent that all samples assessed for AMD will be by nature heterogeneous and will have positive values of CH.

As a result of CH and DH, no matter how well a sample is extracted and prepared, it is likely that any analysis carried out will yield different results to the “true” value.

Detailed methods for estimating CH and DH are given in Pitard (1993) but these methods rely on some simple assumptions about the materials being assessed that cannot be generally applied to waste rock (although may be applied to in situ material prior to mining).

The assumptions include:

- The mineral phase being assessed has a defined density (i.e. restricted to one mineral phase for example pyrite)
- The mineral phase is present in gangue rocks that have a defined density (i.e. assumes for example pyrite present in monolithic quartz gangue)
- The liberation of the mineral phase of interest occurs at an optimum grain size that can be defined
- Shape of the mineral phase can be defined (flakes such as biotite for example compared to cubes of pyrite)

5.0 DETERMINATION OF CONSTITUTION HETEROGENEITY (CH_L)

For the purposes of determining the heterogeneity of a sample and to provide useful information about sampling procedure, it is the heterogeneity between (not within) fragments that we are interested in determining. The objective therefore is to characterise the heterogeneity of a lot (L) with respect to a critical component of a fragment (A_i). The total mass of the critical component (A) in each fragment (i) making up a lot (L) is defined by the fragment mass (M_i) multiplied by the critical content (a_i) in the relation:

$$A_i = a_i M_i \quad [1]$$

The constitution heterogeneity CH of a Lot L is defined as the relative and dimensionless variance of the heterogeneities (CH_L) with respect to the values for A_i carried by the number of fragments (N_F) making up the lot. This is shown in EQ2 where M_i is the fragment mass, M_L is the mass of the entire lot, a_i is the critical component (concentration) of a fragment and a_L is the average value (concentration) of the critical component in the entire lot (L):

$$CH_L = N_F \sum_i \frac{(a_i - a_L)^2}{a_L^2} \cdot \frac{M_i^2}{M_L^2} \quad [2]$$

The CH_L is difficult to calculate in completeness for a given lot because N_F can be very large (for example the number of 3mm gravel fragments in a 5kg crushed sample for example is very large and would require a prohibitive amount of data analysis). To calculate the characteristic of the material making up the lot independently from the size of the lot, CH_L can be multiplied by the average weight of a fragment. This results in determination of the constant factor of constitution heterogeneity IH_L .

$$IH_L = CH_L M_i \quad [3]$$

IH_L has the dimensions of a weight (g). IH_L can always be calculated regardless of the large number of fragments and is used in the calculation of FE.

6.0 DETERMINATION OF FE

The fundamental error variance identified by Gy (1982) is the smallest achievable residual average error, or a loss of precision inherent in the sample due to compositional variability (including particle size, density, chemical composition etc). FE is therefore directly related to CH and DH, and therefore IH_L . According to Gy's work FE is proportional to the cube of the nominal particle size and inversely proportional to the mass of the sample.

Knowing these parameters of FE steps to reduce FE can be deduced as such:

1. Increase the mass of the sample M_S
2. Reduce the particle size (by crushing for example)

Point 1 can be addressed at the sampling stage as larger samples to be taken in the field. Point 2 is addressed as part of sample preparation where particle size reduction can be carried out (i.e. crushing/grinding). On this basis reducing the particle size provides a practical means to reduce FE.

Estimation of the variance of the fundamental error σ_{FE}^2 is given by Gy as follows where M_S is the sample weight and M_L is the weight of the lot:

$$\sigma_{FE}^2 = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) IH_L \quad [4]$$

If a lot has a very large weight compared to M_S then a maximum variance of FE can be calculated:

$$\sigma^2(FE)_{max} = \left(\frac{1}{M_S} - 0 \right) IH_L \quad [5]$$

If the sample M_S has come from a splitting operation (e.g. riffle splitter) then a minimum value for the variance of FE can be calculated:

$$\sigma^2(FE)_{min} = \left(\frac{1}{M_S} - \frac{1}{2M_S} \right) IH_L \quad [6]$$

Using these equations therefore we can determine the appropriateness of the sampling program and give meaningful advice about optimising the sample size.

7.0 SAMPLING APPROACH

The approach to sampling and analysis of heterogeneous materials then becomes very important when FE is considered. Sample sizes for standard AMD tests are generally small. Typically, for ICP analysis a laboratory will extract a small 1-10g sub sample of a parent sample on which to complete analysis. For a NAG test approximately 2g of material is analysed. For a TCLP leach test 100g of material is analysed For paste pH 10g of material is analysed

In addition the selection of the sub sample may take place after sieving or crushing of the parent sample which may introduce preparation biases. This is an important consideration as different tests require different particle sizes of material.

Therefore if FE is significant then clearly it is unlikely that a single 1-10g sub sample of the parent will be representative (chemically or mineralogically) of the sample as a whole.

To illustrate this point an estimation of the sample size required for a toxicity characteristic leaching procedure (TCLP) test is given in Pitard 1993. For a waste sample with maximum particle size of 9.5mm using 100g for the leach test results in a maximum standard deviation

of fundamental error FE of 46%. To be able to reduce this error to $\pm 5\%$ a sample size of 8,574g is required; clearly much larger sample than laboratories can routinely cater for.

There is significant potential for FE to be very large for standard AMD testing given commercial labs use such small sample volumes. Preparation methods may aid reduction in FE, however given the best way to reduce FE is to reduce particle grain size, this is not possible for leach tests which are carried out on material of specific grain size fractions due to increased mobilisation of mineral phases at smaller grain sizes.

8.0 A TYPICAL HETEROGENEITY PROBLEM FOR WASTE ROCK SAMPLING

Figure 1 shows the heterogeneity problem faced when trying to determine how to sample waste material. This 90cm long core from drilling of a waste rock dump weighs approximately 10kg and contains at least 4 material types (based on colour alone). Some common questions would be:

- Should the whole core be retained or sub samples taken in the field?
- Is a single composite adequate?
- If a composite is adequate how large should the composite be?
- Should this core be sub sampled into 4 separate samples?
- Should screening of particle sizes be carried out?
- Should the whole sample be crushed?



Fig. 1. Typical drill core from waste rock dump investigation

Although at first glance the simple answer is that the best method would be to sub sample the entire fraction of each of the 4 main material types, however:

- This may not be feasible due to project costs of completing extremely detailed sampling in this manner.
- It may be that with good laboratory preparation a composite sample may provide adequate results for parameters such as total sulfur
- It may be that the colour does not have strong correlation with the mineral phase of interest (for example sulfide content)

In addition various sampling methods require different sampling preparation.

- Total sulfur analysis requires pulverised material for example ($<100\mu\text{m}$)
- Leach column may use $<6\text{mm}$ material
- Paste pH may use $<2.3\text{mm}$ material

There are therefore increasing amounts of processing work the more the sample is subsampled, and sample volumes are becoming increasingly small (which as we have established can increase FE)

To best tackle this problem one should determine:

- The heterogeneity of the material with respect to the mineral species that we are studying (CH_L)
- The fundamental sampling error (FE) for the proposed sampling and preparation method

A simplified heterogeneity analysis tool has been developed for this task to aid with answering these questions that arise nearly every time waste rock characterisation projects are started.

9.0 SIMPLIFIED HETEROGENEITY ANALYSIS TOOL

A simplified tool has been developed to determine the effects of heterogeneity, to produce heterogeneity profiles for AMD characterisation assessments.

To allow for the large amounts of analysis suggested, a benchtop XRF unit is suggested as a cost effective analysis tool. As has been outlined in this paper it is the FE not the AE that will have the largest impact on producing correct results; therefore the use of analysis tools with lower than laboratory-grade precision can be statistically justified.

A suggested procedure is outlined as follows for the heterogeneity assessment and sampling procedure assessment for a project where a reasonable number (>20 samples) of large (>5kg) samples of waste rock material are collected (Table 1).

It is suggested that at least 5-10 sample lots be subjected to heterogeneity analysis. Sample lots should be selected that are broadly representative of the types of materials gathered from site. This can be based on colour, rock type, density etc.

Table 1. Sampling process for each lot subjected to heterogeneity study

Sample selection	Sample processing	Analysis	Purpose
Sample set 1: 10 small grab samples from the lot, approx. 20-200 g per sample	<i>Crush sample, and pulverise entire sample</i>		Assesses heterogeneity profile for grab samples
Sample set 2: 30-50% material crushed to <6mm	<i>Using splitter, break entire sample down into a large number of sub samples representative of the size of typical laboratory sub samples (50-100g each), pulverise individual samples in full</i>	<i>FPXRF</i>	Estimate FE for sampling method and heterogeneity profile for crushed material
Sample set 3:	<i>Crush each fraction to <6mm. Use splitter to break</i>		

30-50% of material screened through as many sieve sizes as possible, minimum of 3 (2.3mm, 6.7mm, 13.2mm)	<i>each sieved fraction into a large number of sub samples (50-100g each), pulverise individual samples</i>	Assess influence of particle size distribution on heterogeneity profile
Sample set 4: Select at least one of the pulp samples from set 2 and 3	<i>Split pulp sample into a large number of smaller samples approx 5g in weight</i>	Assess effectiveness of pulverising. Use samples obtained to assess AE

10.0 CASE STUDY

A case study is presented based on the following analysis work:

- 2 Drill core samples (approx 90cm long, 8kg in weight) from AMD waste rock dump characterisation investigation were subject to detailed analysis
 - Core A contains material that is visually heterogeneous, and contained visual evidence of sulfides/sulfates
 - Core B contains material that is visually homogeneous and does not have evidence of sulfides/sulfates
- Approximately 3kg of material from each core was run through 15 stage sieve sorting with standard sieve sizes ranging from 0.075mm to 26mm. Each fraction was then crushed in a rock crusher to <6mm, and 50g (where enough material was present) sub sample was obtained using a riffle splitter. The 50g sample was then pulverised.
- Approximately 1.5kg material from each core was crushed to <6mm in a rock crusher. The crushed material was then entirely split using a rifle splitter into approximately 65 samples of 20g each. Each of these samples was pulverised.
- 10 grab samples (25g) were taken from each core before processing occurred at 10cm intervals.
- One pulp sample from Core A and Core B was subject to micro-splitting to approximately seven, 6g sub samples.

The aim of the study was to allow detailed heterogeneity assessment of the two samples of waste materials as part of an assessment of the suitability of the current sampling and analysis program.

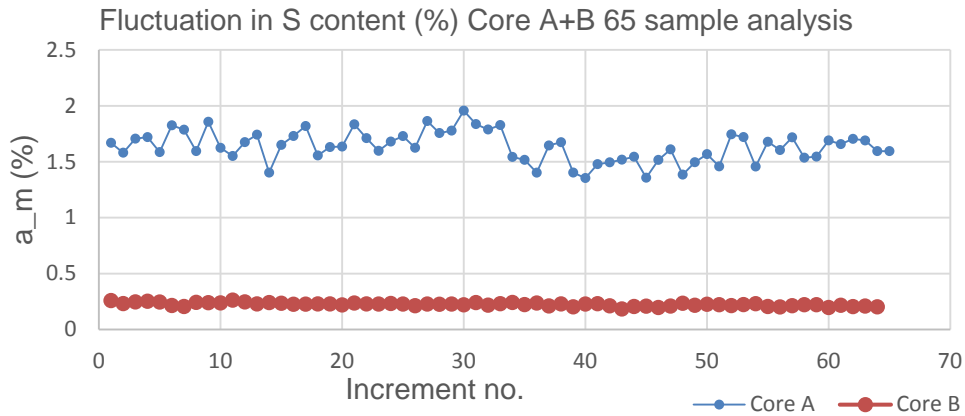


Fig. 2. Sulfur content (a_m %) in 65 sub samples (20g each) from complete analysis of 1.5kg of crushed material from Core A and Core B.

Figure 2 shows the results of the 65 sample analysis of the <6mm crushed material samples of Core A and B. It is clear that Core A has higher sulfur content and appears to have higher variability with respect to intra-sample heterogeneity given the range of fluctuations in S content appears higher. In general the results indicate that the process of riffle splitting appears to produce samples that are reasonably consistent for both cores.

Figure 3 shows the same data plotted as a heterogeneity chart (where h_m is the dimensionless value for variance in heterogeneity which is equal to the variance of the sample critical content from the weighted average critical content for the lot) . It is clear that although Figure 2 indicates Core A to have higher intra-sample variability, when the concentration data is plotted on a relative scale the variance in heterogeneity is actually very similar between the two cores.

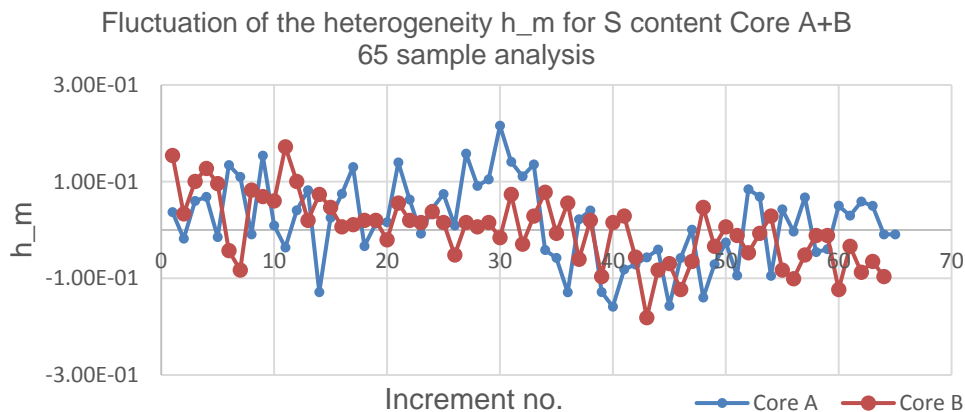


Fig. 3. Heterogeneity profile for 65 sample analysis from Core A and Core B

Table 2. 65 sample heterogeneity analysis Core A+B

	Core A	Core B
M_L (g)	1300	1280
A_L (mg)	2092	286
a_L %	1.609597	0.223578
M_m(avg) (g)	20	20
CH_L	0.007258	0.004752
IH_L (g)	0.145165	0.095047
$\sigma^2(FE)_{min}$	+8.6%	+6.8%

Table 2 shows that

- As expected the calculated values for weighted average concentration (a_L) of S is much higher for Core A.
- The value A_L is given because this indicates the total amount of S in the sample which can be more useful than a concentration to calculate acid loading.
- M_m is the average weight of an individual sample.
- Values for CH_L and IH_L are quoted, although this is not the CH_L of the raw material as samples have been processed, the value is useful as a metric to gauge the relative heterogeneity of the sub samples obtained. Core A can be seen to have a higher intra-sample heterogeneity given CH_L is higher than Core A.
- The minimum variance of fundamental error can be seen to be close between the 2 cores and less than 10% in both instances indicating that taking a 20g sub sample by riffle splitting crushed material (<6mm) for S analysis would produce an adequate result for characterizing S concentration in either material lot.

The minimum variance of the fundamental error related to obtaining a 20g sample from the whole lot was calculated using Eqn. [6], the working for Core A is shown below:

$$\sigma^2(FE)_{min} = \left(\frac{1}{20} - \frac{1}{1300} \right) 0.15 = 0.007 \quad [7]$$

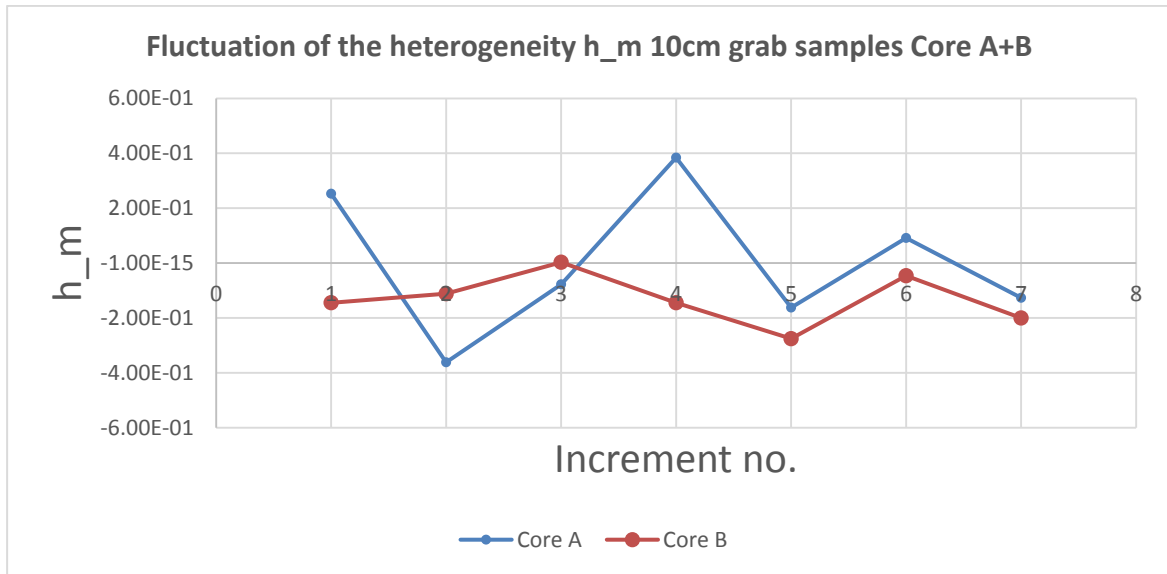


Fig. 4. Heterogeneity profile for 10cm grab sample analysis from Core A and Core B

Figure 4 shows the heterogeneity profile for the 25g grab samples taken at 10cm intervals along each core. It is clear that samples from Core A have a higher degree of heterogeneity than Core B.

Table 3. 10cm grab sample analysis

	Core A	Core B
M_L	175	175
A_L	292.4753	46.375
a_L %	1.671287	0.265
M_m(avg) (g)	25	21.875
CH_L	0.056998	0.011164
IH_L (g)	1.424945	0.244215
$\sigma (FE)_{min}$	24%	9.8%

Table 3 shows that:

- The values for a_L are close for both cores relative to the values given in Table 2 from the 65 sample analysis, indicating that (perhaps surprisingly) taking 9 grab samples produces a reasonably accurate estimation of the mean S grade.
- The value for CH_L in this instance reflects spatial variation I heterogeneity. S content within Core A has a high degree of variability with depth (related to layering of materials with different S content)
- The minimum variance of the fundamental error is significantly higher in Core A at 24% than Core B 9.8% which is indicated from Figure 4.
- The minimum variance of the fundamental error for Core A is much higher than that given in Table 2 which indicates that taking small numbers of grab samples is likely to

be a poor sampling technique for this material. The value for Core B is lower at 9.8% but this is still significantly higher than that given in Table 2 so that, although the material has a lower degree of heterogeneity, grab sampling is still not recommended as good sampling technique.

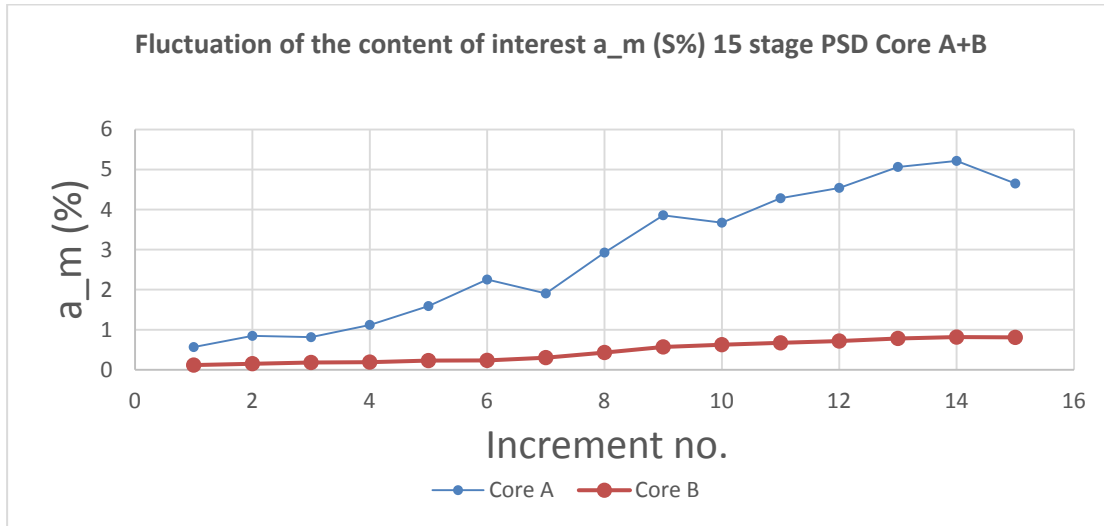


Fig. 5. Concentration profile for S% in 15 stage PSD analysis from Core A and Core B

Figure 5 shows the fluctuation of S concentration relative to particle size class. Increment 1 is the largest (26mm) particle size and 15 is the smallest (0.075mm). A very strong relationship is noted between particle size and S concentration with concentrations being more than 5 times higher at smaller particle sizes. This is an important observation as it shows that the materials have strong partitioning effects with respect to S and particle sizing (analysis was completed on pulverized samples which negates the influence particle size can have on XRF analysis).

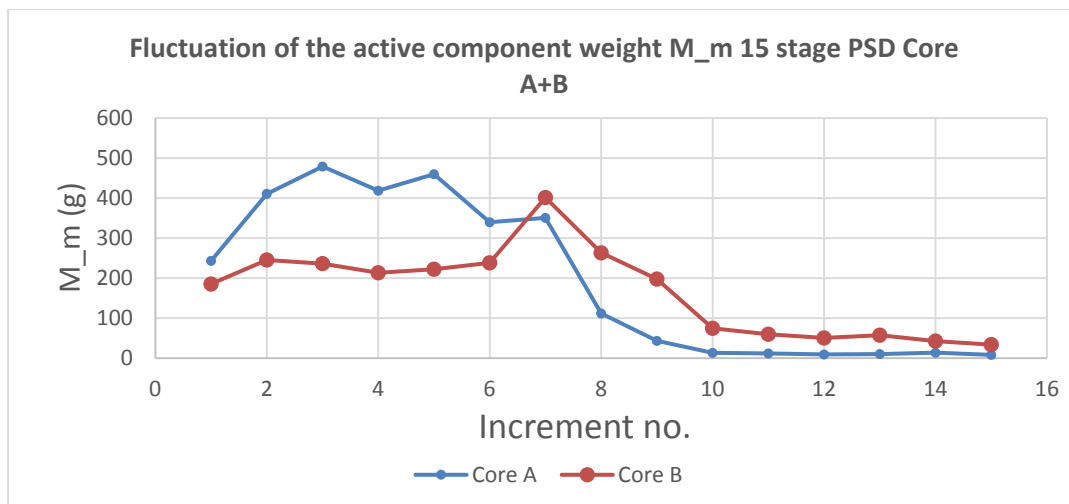


Fig. 6. Sample weight profile for 15 stage PSD analysis from Core A and Core B

Figure 6 shows the weights of each of the particle size classes. It is clear that, as with S concentration, there is strong influence of particle size with smaller particles having much smaller mass contributions in both cores.

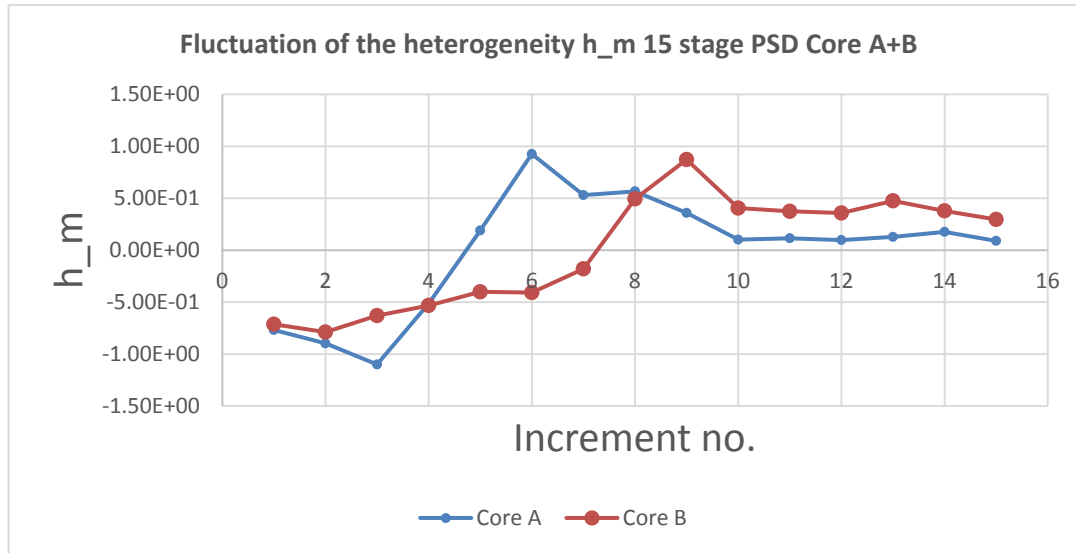


Fig. 7. Heterogeneity profile for S% in 15 stage PSD analysis from Core A and Core B

Figure 7 shows the heterogeneity profile for both cores with respect to the 15 stage PSD. Both cores have a similar profile. It should be noted that the values for h_m are significantly higher for this graph than others presented indicating heterogeneity is very high with respect to S concentration and particle sizing. It is interesting to note that Figure 5 appeared to show Core A had the higher degree of heterogeneity but re-scaled both cores appear to show similar levels of heterogeneity related to particle size.

Table 4. 15 stage PSD fraction analysis Core A+B

	Core A	Core B
M _L	2921.6	2521.4
A _L	4298.311	823.3702
a _L %	1.471218	0.326553
M _m (avg) (g)	194.7733	168.0933
CH _L	0.305581	0.270901
IH _L (g)	59.51895	45.53662
$\sigma (FE)_{min}$	117%	89.4%

Values for the minimum variance of the fundamental error were calculated related to obtaining a 50g sample (which is the smallest sub sample that can be obtained selecting material at the largest size fraction).

Table 4 shows that:

- A_L values are close to those given in table 2, this is not surprising as it may seem though as although heterogeneity is high in this experiment, the average S content of the lot can be expected to be consistent given the weighted method of calculating S content using A_L and M_L.
- CH_L and IH_L values are significantly higher for both cores confirming the extreme heterogeneity distribution of S within particle size class
- Values for the minimum variance of the fundamental error are similar between the two cores indicating the partitioning of S is similar between the two materials. Values of over 80% for Core B and over 100% for Core A indicate that selectively sampling a particle size fraction for S analysis will have extreme influence on the representativeness of the results.

Table 5 shows the distribution of S as weighted percentages within the size fractions. The proportion of the S content derived from the <2.36mm size classes is 27% of the total S content derived from only 17.3% of the sample weight. The top size fractions 13.2-26mm in comparison contribute only 20% of S for 39% of the sample weight.

Table 5. 15 stage PSD fraction analysis Core A, S distribution

PSD fraction	% of total weight	Sample weight fraction % total
26	3.197507	8.320783
19	8.075447	14.05737
13.2	9.0513	16.38828
9.5	10.89784	14.32092
6.7	17.00343	15.73795
4.75	17.79972	11.62719
2.36	15.53777	12.00027
1.18	7.596266	3.819825
0.6	3.868454	1.475219
0.425	1.127871	0.451807
0.3	1.165889	0.400465
0.212	0.961663	0.311473
0.15	1.202046	0.349124
0.075	1.638368	0.462076
-0.075	0.876426	0.277245

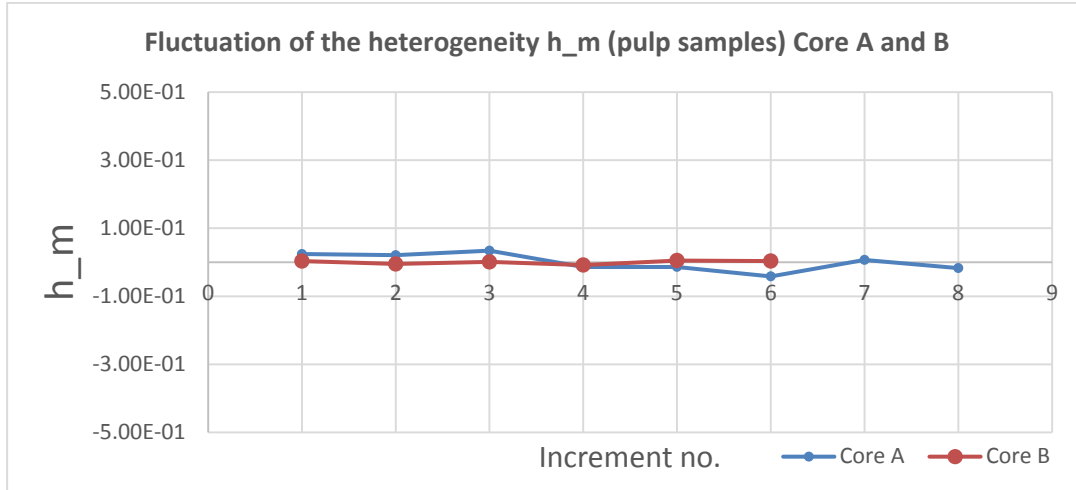


Figure 8: Heterogeneity profile for S% in pulp sample analysis from Core A and Core B

Table 6. Pulp analysis Core A+B

	Core B	Core A
M_L	56	36
A_L	20.32073	51.17106
a_L %	0.36287	1.421418
M_m(avg) (g)	7	6
CH_L	0.000575	2.41E-05
IH_L (g)	0.004023	0.000145
$\sigma (FE)_{min}$	0.08%	0.08%

Figure 8 shows the heterogeneity profile for the micro-analysis of pulp samples. For both cores heterogeneity is very low which is expected given that pulverizing samples is known to significantly reduce $\sigma (FE)_{min}$ as a result of size reduction. From table 6 the variance of the fundamental error is very low for both cores and indicates:

- The pulverizing step carried out introduces a very small amount of error
- The XRF analysis must have a high level of precision to be able to produce this extremely low value for $\sigma (FE)_{min}$

11.0 CONCLUSIONS

The results presented in this paper are a small fraction of the data that OKC has gathered using this profiling tool in conjunction with utilization of bench top XRF analysis.

From the research carried out, heterogeneity has been demonstrated to be a significant factor controlling the fundamental sampling error, and thus the ability to produce analytical results that are representative when dealing with waste rock materials. A profiling tool has been presented which allows heterogeneity to be studied both in the context of the impact on the fundamental error during the sampling process, and with respect to the properties of the material. General findings from utilization of the profiling tool include:

- Heterogeneity is shown to be very high with respect to 'grab' sampling from different depths of core material and from different particle sizes. Extreme care is therefore required when interpreting the results of either:
 - Grab sampling of small samples
 - Samples that have been screened for particle size fractions
- Crushing samples of around 1-3kg of material to a grain size of <6mm and using riffle splitting to take small sub samples (20g) for analysis appears to result in acceptable levels of fundamental sampling error. However it is recommended for any sampling program that as large a sub sample as possible be taken as the larger the sample the lower the fundamental error will become.
- The lowest value for the variance of the fundamental sampling error for any of the sampling techniques has been found to be around 6.8% for crushing to <6mm and riffle splitting, this is a minimum so the actual errors are likely to be higher.
- Selecting a 50g sample based on particle size has been shown to have the highest value for the minimum fundamental sampling error of 117%.
- To achieve the high volumes of analysis required for these types of intensive analysis studies, low cost analysis techniques are required. Benchtop XRF has been demonstrated to be a very useful tool for this purpose.
- As is commonly known, pulverizing material produces samples with extremely low levels of heterogeneity and therefore the larger the sample that is pulverized the lower the fundamental error will become.
- Selecting very small samples (<10g) of material that has not been pulverized for analysis, and has been size selected as is the case for commercial analysis like paste pH (which is done on <2.3mm fraction), is very likely to introduce very large fundamental sampling errors

5.0 REFERENCES

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