Stability under transport; an experimental study of OREAS CRMs

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Background

The stability of reference materials (RM) under transport conditions is also known as 'short-term stability'. For the purposes of this study, we take a look at whether any changes can be measured from the time packaged RMs leave the suppliers warehouse to the time it takes to arrive at the user's premises. We are also assuming that any change to the packaged RM unit will be physical in nature, through the phenomenon of particle segregation.

The occurrence of particle segregation is well known by scientists where, by virtue of differences in size and physical property (volume, density, shape, etc), particles will differentially move (segregate) from one location to another. This is particularly important for metal concentrations in RMs given that the sample provided is typically sub-sampled for analysis which may or may not be representative of its true concentration. Particle segregation is particularly ubiquitous during powder handling and transfer and is most pronounced in free-flowing powders. Powders that tend to agglomerate are inherently not free flowing and exhibit high levels of cohesion and adhesion. This 'sticky' manifestation can only be overcome by mixing devices that employ high shearing forces or subject the powder to impact. However, when these types of powders have been mixed (homogenised) they are far less susceptible to segregation due to the high inter-particulate forces that resist inter-particulate motion that leads to unmixing.

A likely real-world context for particle segregation would be under road transport conditions. The low and high frequency vibrations from the moving vehicle traveling along a highway can pass these vibrations to a jar of powder and unmixing can occur leading to segregation. Likewise, if a jar is handled and bumped many times; For example, taken from a shelf and placed on a bench to be subsampled in a repeated manner over the course of a year or so.

Road transport conditions can also be artificially simulated and accelerated using commercial vibration platforms such as a paper jogger. The high frequency vibrations cause the particles within the powder to vibrate and will initiate particle segregation if the physical attributes of the powder allow.

Hypothesis

1.2 litre jars of OREAS CRMs (pulps) are inherently resistant to segregation and will not unmix when placed on a commercial vibration platform for a period of 30 seconds or 5 minutes. A sample from the top section of the jar will be no different in its chemical and physical signature to a sample from the bottom section of a jar.

Experimental design

In order to capture segregation affects across a range of different material types, four different OREAS CRMs were selected. These CRMs were chosen to be as different as possible from one another on the basis of their chemistry, physical grain size populations and metal concentrations. Three of the selected CRMs were comprised of gold ore and one of iron ore. Gold (Au) concentrations ranged from 0.39 to 7.66 ppm covering a variety of matrices (oxide, intrusive and meta-volcanic). The grain size populations of these CRMs also varied markedly from 10-90% minus 30 microns. The hematitic iron ore CRM was prepared to a coarser gain size specification compared to the gold ore CRMs as shown in Table 1 below.

Table 1. OREAS CRMs used for particle segregation study.

CRM ID	Element (UOM)	Mass in jar	Matrix	Particle size distribution
OREAS 905	Au: 0.391 (ppm)	1000g	Weathered rhyodacite	>10% minus 30 µm; Remainder is 98% minus 75 µm.
OREAS 622	Au: 1.85 (ppm)	1000g	Rhyodacite	>90% minus 30 µm; Remainder is 98% minus 75 µm.
OREAS 256	Au: 7.66 (ppm)	850g	Weathered greenstone/ basaltic scoria	>50% minus 30 µm; Remainder is 98% minus 75 µm.
OREAS 40	Fe: 66.7 (wt.%)	1000g	Hematitic	98% minus 75 µm

*UOM = unit of measure; SI unit equivalents: ppm (parts per million) ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% (weight per cent).

The four OREAS CRMs were packed into 1.2L plastic jars with each jar holding 850 or 1000g of material and subjected to vibration using a Syntron® J-50-B Jogger (see Figure 1). One set of jars was subjected to 30 seconds of vibration and another identical set was subjected to 5 minutes of vibration.

Figure 1. Vibration platform with jar of OREAS 256.

Following vibration, the top and bottom section of each jar was subsampled. The bottom section was subsampled by cutting the bottom ~20mm profile away using a knife and then carefully removing the top material in order to obtain multiple small subsamples from different areas of the base (Figure 2) to makeup a 60g sample weight.

Figure 2. Base of jar being cut and subsampled.

This process was repeated for each jar generating 16 samples as per Table 2.

Table 2. OREAS CRM subsamples for segregation study.

CRM ID	Vibration time	Sample location	Analysis
OREAS 905	30 sec	Top	Au and PSD
OREAS 905	30 sec	Bottom	Au and PSD
OREAS 905	5 min	Top	Au and PSD
OREAS 905	5 min	Bottom	Au and PSD
OREAS 622	30 sec	Top	Au and PSD
OREAS 622	30 sec	Bottom	Au and PSD
OREAS 622	5 min	Top	Au and PSD
OREAS 622	5 min	Bottom	Au and PSD
OREAS 256	30 sec	Top	Au and PSD
OREAS 256	30 sec	Bottom	Au and PSD
OREAS 256	5 min	Top	Au and PSD
OREAS 256	5 min	Bottom	Au and PSD
OREAS 40	30 sec	Top	Fe and PSD
OREAS 40	30 sec	Bottom	Fe and PSD
OREAS 40	5 min	Top	Fe and PSD
OREAS 40	5 min	Bottom	Fe and PSD

PSD = Particle Size Distribution

For Au in OREAS 905, 622 and 256 (Tables 3 to 5 below), seven 60g samples of each CRM were sent to the Intertek laboratory in Manila, Philippines for analysis of Au. The seven samples consisted of three control samples (inserted at the start, middle and end of the sample sequence) and four experimental samples. Each 60g sample was fired in duplicate and read in triplicate using method FA30 (30g fire assay with AAS finish).

Student's t-test is used with *p*-values (at a significant level of 0.05) to test for statistically significant difference between two independent means; that is, that each experimental mean is either greater than, or less than, the Control Mean. In this context, if particle segregation were to occur, the bottom section of each jar would accumulate more gold (Au) relative to the top section of the jar. The same would be true for Fe in OREAS 40. Furthermore, the 30 seconds of vibration would more likely show a weaker particle segregation affect compared with the 5 minutes of vibration.

The null hypothesis (H_0): $Au_c – Au_{xx} = 0$, stipulates that there is no statistically significant difference between the Control mean (Au_c) and the experimental means, where Au_{xx} is the mean of the experimental samples ($Au_{30s\text{-}t}$, $Au_{5m\text{-}t}$, $Au_{30s\text{-}b}$ and $Au_{5m\text{-}b}$, respectively).

We can design the appropriate one-tailed tests for the alternative hypotheses as follows:

1. $Au_c > Au_{30s\text{-}t}$
2. $Au_c > Au_{5m\text{-}t}$
3. $Au_c < Au_{30s\text{-}b}$
4. $Au_c < Au_{5m\text{-}b}$

where,

Au_c is the mean Au concentration of the control samples;
$Au_{30s\text{-}t}$ is the mean Au concentration of the 30sec-top samples;
$Au_{5m\text{-}t}$ is the mean Au concentration of the 5min-top samples;
$Au_{30s\text{-}b}$ is the mean Au concentration of the 30sec-bottom samples;
$Au_{5m\text{-}b}$ is the mean Au concentration of the 5min-bottom samples;

For Fe in OREAS 40, (Table 6 below) seven 60g samples were submitted for analysis of Fe at the Bureau Veritas laboratory in Perth, Australia. The seven samples consisted of three control samples and four experimental samples but only single analyses were undertaken due to the extra precision of this method. This precluded the calculation of standard deviations and the ability to conduct t-tests so the Median Absolute Deviation (MAD) method was used instead. This method highlights anomalous results using z-scores (rejected if $z_i > 2.5$) computed from the robust estimators of location and scale, T and S, respectively, according to the formulae:

$$z_i = \frac{x_i - T}{S}$$

where,

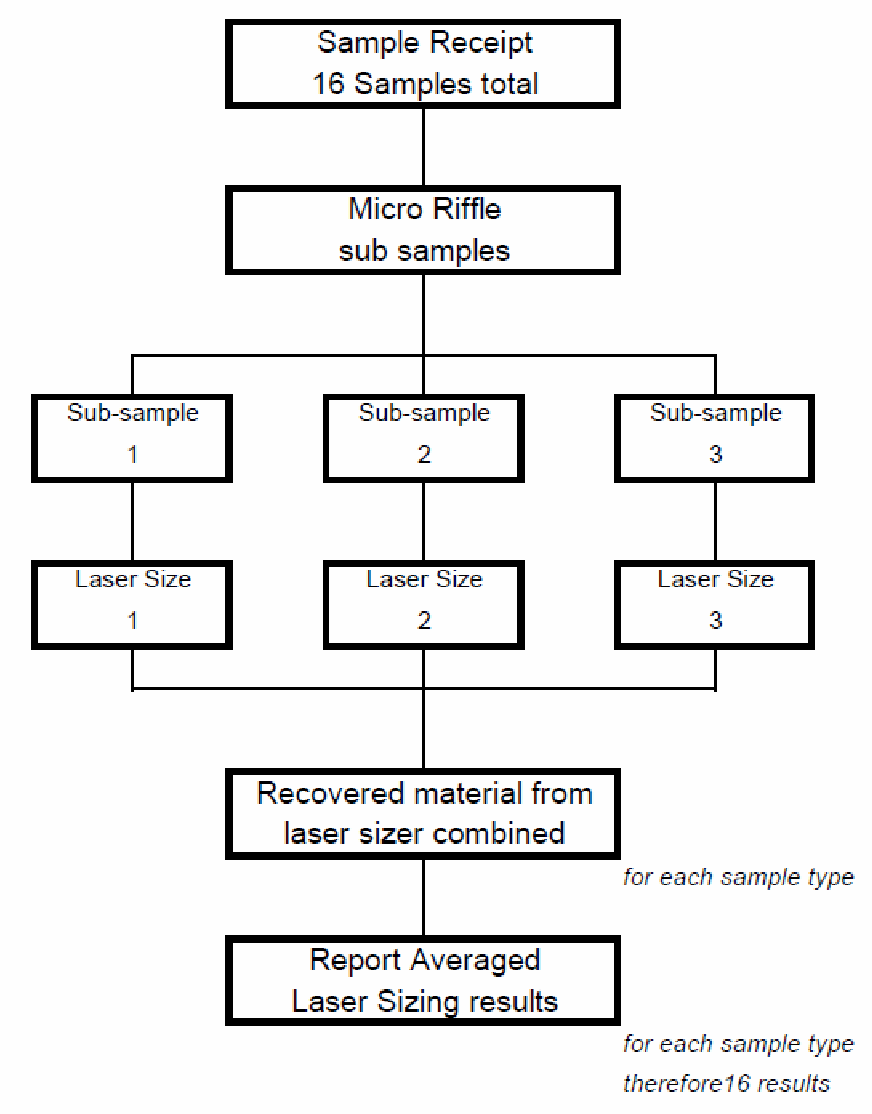
T is the median value in a data set;
S is the median of all absolute deviations $|\Delta j|$ from the sample median multiplied by 1.483, a correction factor to make the estimator consistent with the usual parameter of a normal distribution.

$$\text{I.e. } S = 1.483 \times \underset{j=1\ldots..n}{median} \mid \Delta j \mid$$

$$\text{where } \Delta = \underset{i=1\ldots..n}{xi - median(xi)}$$

Particle Size Distribution's (PSD's) were also assessed for each experimental sample as per Figure 3 below. For this work, 10g samples were submitted to the Bureau Veritas laboratory in Adelaide, Australia. Each 10g experimental sample was micro-riffled into 3 subsamples to obtain an average PSD using a Malvern Mastersizer 2000.

Figure 3. Particle size analysis showing steps.



Results

The results for the comparison of differing metal concentrations between the experimental samples and control samples are summarised in Tables 3 to 6 for OREAS 905, 622, 256 and 40, respectively. Tables 3 to 5 below do not show any statistically significant *p*-values ($p < 0.05$) and Table 6 does not show any significant z-scores ($z > 2.5$). These results support the null hypothesis. That is, following 30 seconds or 5 minutes of vibration, a sample from the top section of the jar is no different in its chemical signature to a sample from the bottom section of a jar.

Table 3. OREAS 905 – comparison of Au for ‘top’ and ‘bottom’ subsamples at 30 sec and 5 min.

Sample	Mean	*p*-values
30sec-top	0.4088	0.50
5min-top	0.4086	0.47
30sec-bottom	0.4091	0.43
5min-bottom	0.4088	0.50
Control	**0.4088**	

Table 4. OREAS 622 – comparison of Au for ‘top’ and ‘bottom’ subsamples at 30 sec and 5 min.

Sample	Mean	*p*-values
30sec-top	1.868	0.12
5min-top	1.870	0.15
30sec-bottom	1.878	0.31
5min-bottom	1.873	0.21
Control	**1.885**	

Table 5. OREAS 256 – comparison of Au for ‘top’ and ‘bottom’ subsamples at 30 sec and 5 min.

Sample	Mean	*p*-values
30sec-top	7.518	0.12
5min-top	7.595	0.10
30sec-bottom	7.567	0.46
5min-bottom	7.581	0.24
Control	**7.561**	

Table 6. OREAS 40 – comparison of Fe for ‘top’ and ‘bottom’ subsamples at 30 sec and 5 min.

Sample	Mean	z-score
30sec-top	66.64	0.27
5min-top	66.62	1.08
30sec-bottom	66.61	1.48
5min-bottom	66.65	0.13
Control	**66.65**	

Results for the comparison of particle size distributions (PSD) for the four experimental samples for each CRM are schematically shown in Figures 4 to 7 for OREAS 905, 622, 256 and 40, respectively. The red, green, blue and dark blue lines represent the four different experimental samples as per the LEGEND of each graph and are almost perfectly superimposed on one another. This indicates the difference in particle size distributions between the four experimental samples for each CRM is negligible and we can conclude that each sample is drawn from the same population.

Figure 4. PSD for OREAS 905.

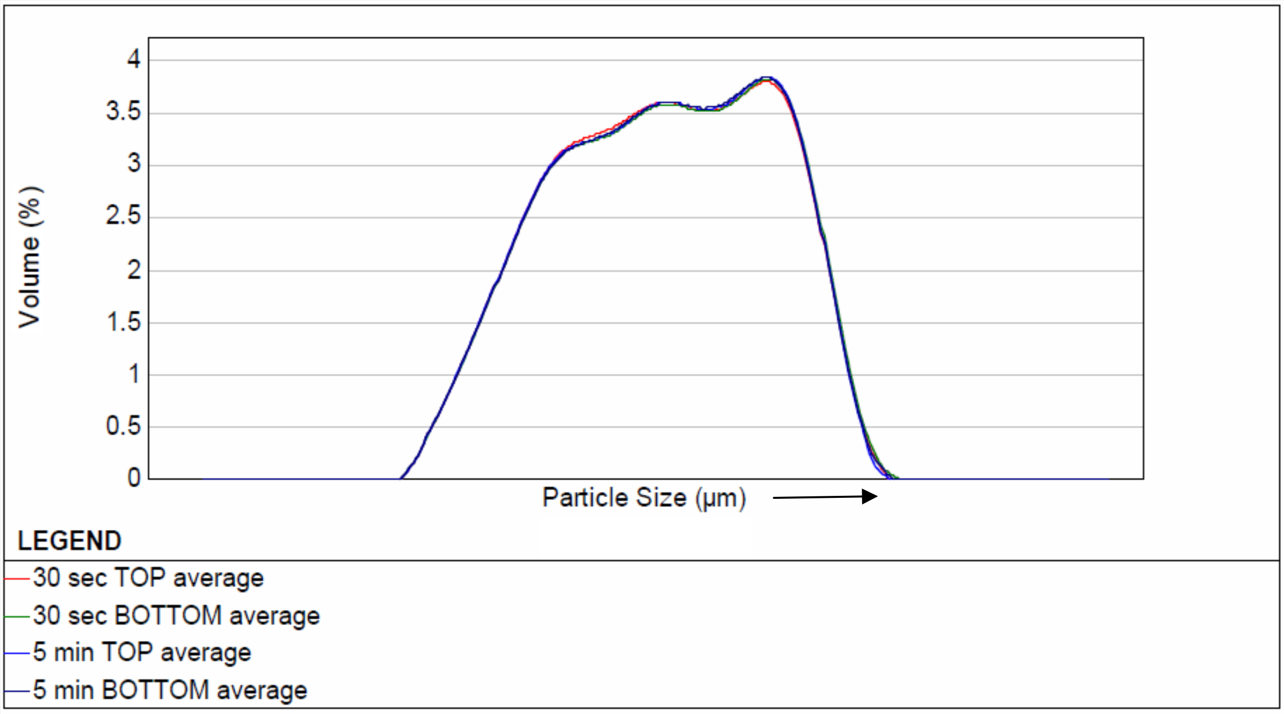


Figure 5. PSD for OREAS 622.

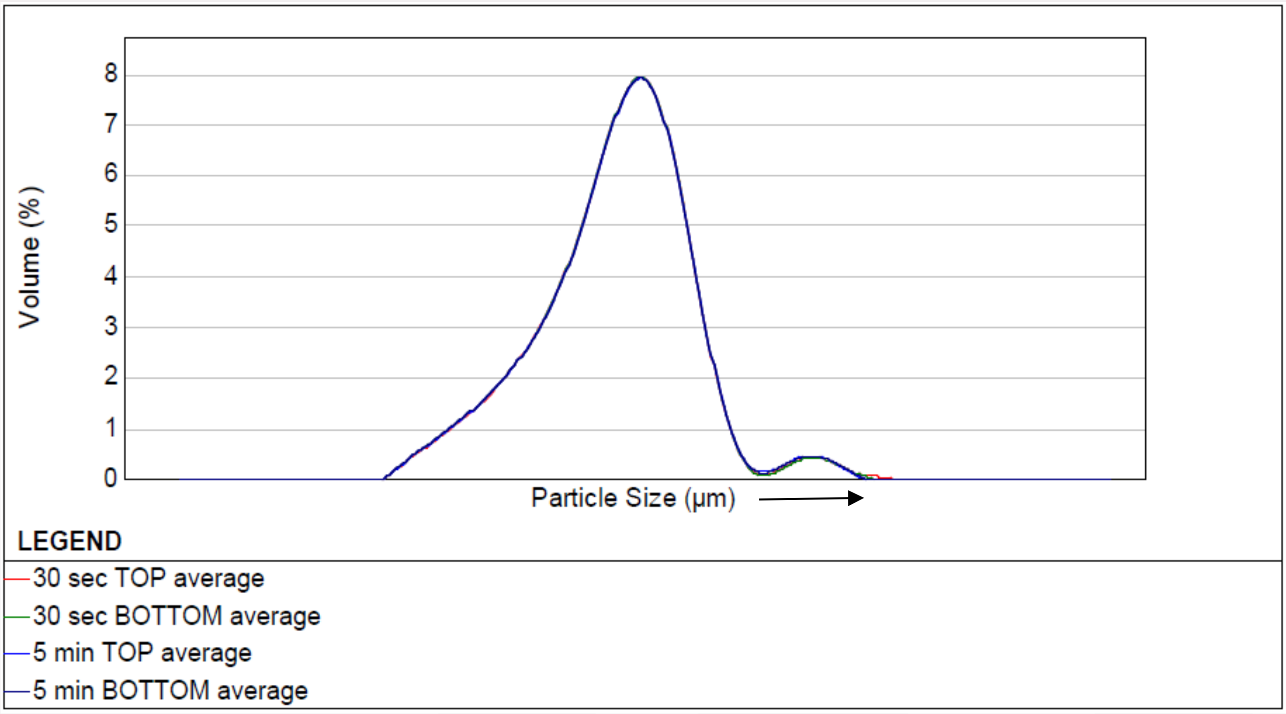


Figure 6. PSD for OREAS 256.

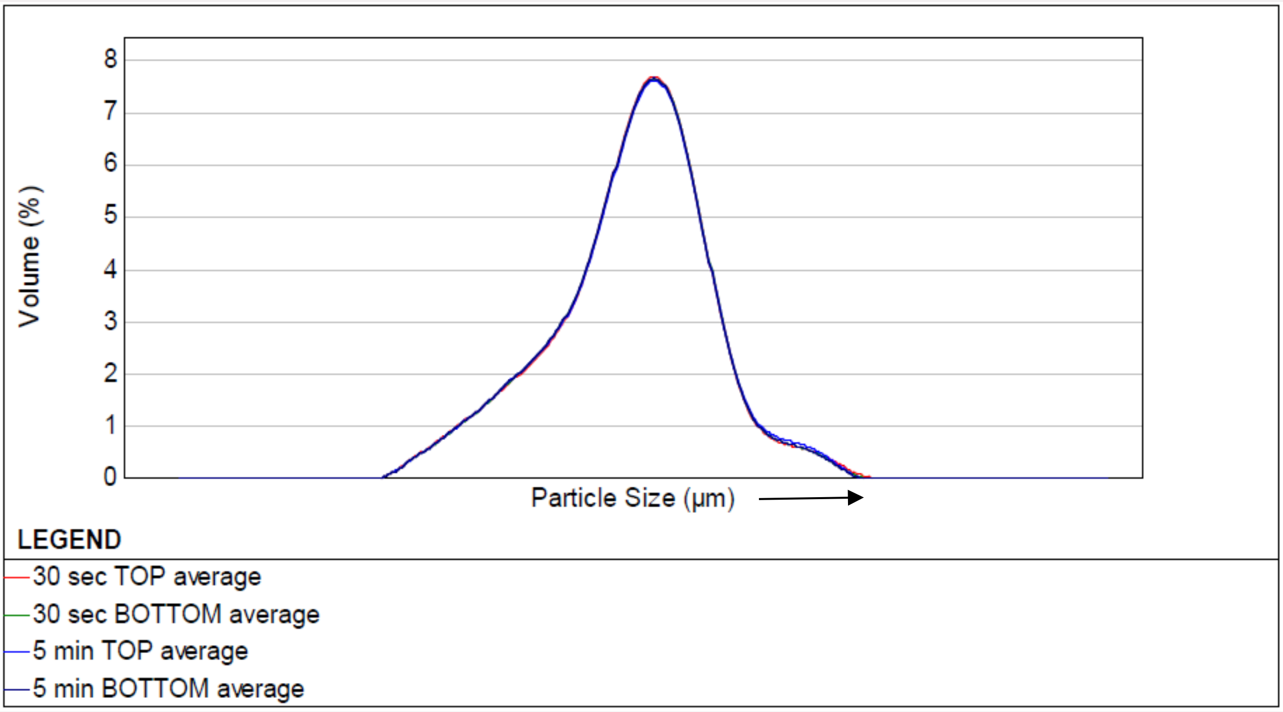
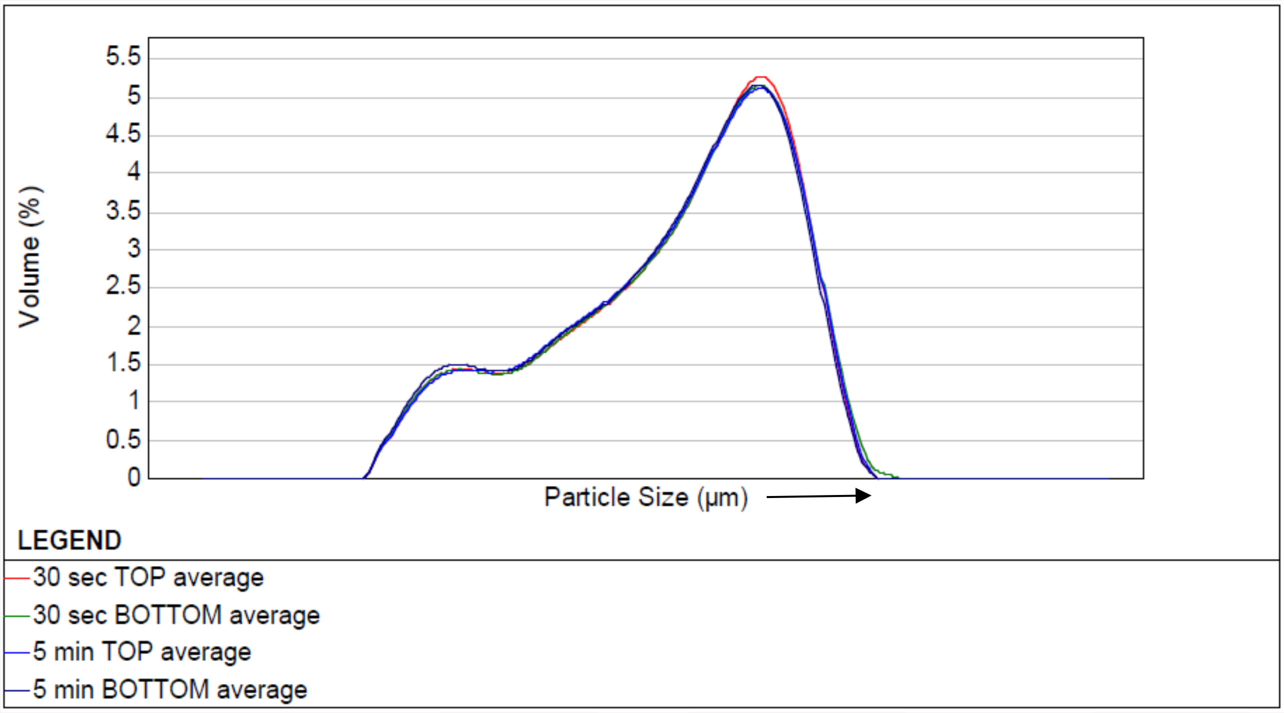
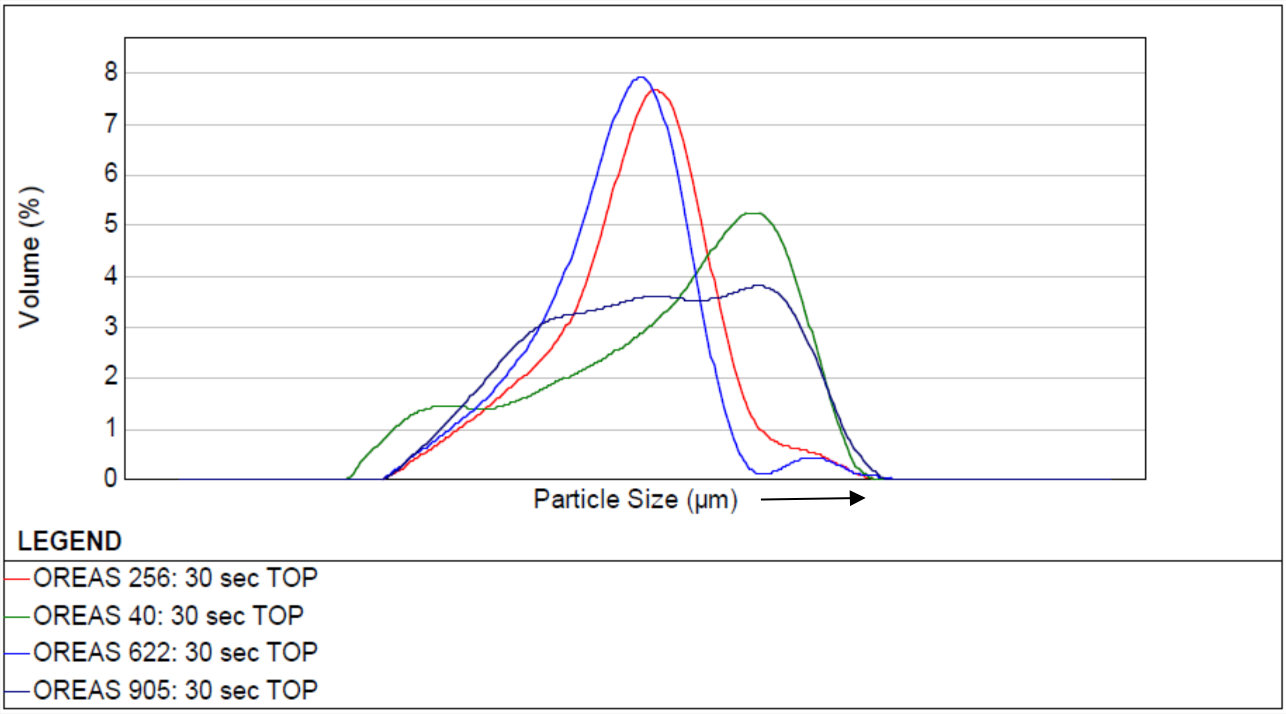


Figure 7. PSD for OREAS 40.



To facilitate an appraisal of PSD's between the four CRMs Figure 8 has been included and shows that OREAS 40 (iron ore) has the widest distribution of grain size with both a higher portion of coarse particles (presumably overrepresentation of hematite) and higher portion of fine particles (presumably overrepresentation of aluminosilicate clays). OREAS 905 shows the most even spread of grain sizes and OREAS 622 and 256 are very similar to one another with 256 only slightly coarser (right-shifted) in grain size.

Figure 8. PSD for OREAS 256, 40, 622 and 905.



Conclusion

Four different OREAS CRMs were packed into 1.2L plastic jars and studied for segregation affects following 30 seconds and 5 minutes of vibration on a commercial vibration platform (Syntron® J-50-B Jogger). 60g subsamples were taken from the top and bottom sections of each jar and sent for chemical (Au or Fe analysis) and physical (particle size distribution) analysis.

The chemical results between control and experimental samples showed no statistically significant difference in Au concentration based on t-tests with *p*-values (OREAS 905, 622 and 256) at the 0.05 significance level nor was any significant (>2.5) z-score detected for differences in Fe concentration in OREAS 40.

Furthermore, the results for each CRM from a study of particle size distributions comparing the four experimental samples with one another (Figures 4 to 7 for OREAS 905, 622, 256 and 40, respectively) show no evidence of material difference based on a graphical observation of the distribution curves.

The high-quality of preparation and homogenisation of the OREAS CRMs under study account for the absence of particle segregation following short and long periods of artificial vibration. The CRMs have been prepared in such a way that high interparticulate forces dominate and resist interparticulate motion that can lead to unmixing. The immediate onset of vertical vibration is accompanied by compaction of the rock powder where smaller particles fill the interstitial spaces of the larger particles. This behaviour further impedes segregation and any free-flowing tendency of the powder.