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Technical Publication

A Practical Approach to Predicting Ash Deposition

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INTRODUCTION

In recent years there have been major advances in the understanding of ash deposition in combustors. This understanding has come about through development and application of advanced analytical techniques (1,2,3) combined with some excellent experimental techniques (4,5). However, while this detailed fundamental approach has given insight into ash behavior the application of the results with respect to ash deposition has received limited attention. This is unfortunate as the application of the fundamental data can give rise to more accurate predictions of ash deposition. This is even more important in a very competitive utility market where the industry can not afford costly coal contracts combined with an unforeseen number of unscheduled outages.

This paper aims to present the basic principles of ash deposition and how one can use these principles to develop accurate and relevant methods to predict the behavior of ash. Some introduction to the fundamental principles are required. This going back to basics has the advantage that the eventual methods developed will not be fuel dependent or combustor dependent. This will allow both the ability to accurately 'screen' fuels as well as development of methods to economically utilize poorer quality or off-design coals. Furthermore, with a fundamental grounding one can look at coal blends, beneficiated coals, and cleaned coals, as well as different modes of utilization such as gasification, coal water slurry firing, sorbent injection, and fluidized bed combustion.

Despite years of activity in developing an accurate prediction technique it has to be concluded that there is no single simple method. Each one, be it empirical, semi-empirical or fundamentally based has draw-backs. The development of a single method which gives a simple prediction has to be discouraged. These methods, such as the base/acid ratio, fouling index, ash fusion temperatures, have their uses and their proponents. However, they must be used with care in order to make adequate assessments of ash deposition. Unfortunately this rarely happens. Therefore, it is important to stress that it is the following approach that is crucial. From this approach, methods directly applicable and validated by experiment and testing to fouling and/or slagging can be developed. These methods will be better understood by utility personnel than methods inherited or borrowed from other sources.

This paper describes the approach and gives insight as to how it can be used by utilities. The critical parts are coal mineralogy, mineral transformation during coal combustion, initial deposition, and deposit growth/development of strength. In order to obtain a workable approach various assumptions and approximations need to be made. These assumptions and approximations will be discussed. The philosophy behind the approach is simple. How can the formation of thick dense deposit from micron size coal mineral grains be explained or predicted?

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COAL MINERALOGY

Coal is itself a mineral. Associated with this mineral are inorganic minerals which will form ash as the residue of the combustion process. The number of different minerals detected in coal is well over 100. However, for most coals, study and comparison of the coal mineralogy with the coal ash chemical composition indicates that only the major mineral need be considered to adequately describe the coal ash chemistry. That is, the bulk of the ash is represented by the major mineral species. These minerals and their major component oxides are listed in Table 1. Included in the Table are carboxylic acid salts. These represent the organically bound components present in some western fuels. In these coals a significant amount of the calcium, sodium, and magnesium can be bound to the coal matrix as salts of carboxylic acids.

The mineralogy is important as it controls the characteristics of the resulting ash particles. Therefore the coal mineralogy has to be accurately determined. This involves advanced analytical techniques such as Computer Controlled Scanning Electron Microscopy (CCSEM) (2). This technique is able to establish the relative amount of the various mineral phases, the size distribution as well as a semi-quantitative chemical composition. The semi-quantitative chemical composition is used to establish the mineralogy of the detected grain. Also included in the data is the shape of the various particles. Table 2 shows some of the typical output from a CCSEM analysis for a bituminous coal. Further, more detailed analysis can be performed to establish the association of the various minerals within the coal. This would determine if the coal mineral is inherent or extraneous to the coal particle and what minerals, if any, a specific mineral phase is associated with. As western fuels may have significant amounts of key elements organically bound to the coal matrix it is important to supplement the CCSEM analysis with chemical fractionation (6). Chemical fractionation determines the relative amount of selected element in various forms in the coal by a series of leaching experiments. Organically bound elements are leached from the coal with water or ammonium acetate. Elements bound to minerals are usually either retained in insoluble mineral phases or in acid-soluble minerals. For our purposes the chemical fractionation is used only to establish the organically bound fraction of the major elements in the coal.

The detailed analysis of the coal establishes the following:

 o Relative amount of mineral phases

 o The size distribution of these mineral phases

 o The chemistry of the mineral phases

 o The association of the minerals within the fuel

 o Relative amount of organically bound elements (mainly western fuels)

The CCSEM analysis is performed on as-fed coal. This allows the determination of the above data to be directly applicable to coal feed and hence the ash behavior.

MINERAL TRANSFORMATIONS

Having established the coal mineralogy of the as-fed material we can proceed to the next stage. What happens to the minerals during combustion of the coal? The various processes that occur are complex and are still the subject of extensive study. We are concerned with the processes that involve the major mineral species and specifically the processes which will affect the ash formation/growth processes. These processes include fragmentation, melting, reaction, recrystallization, and thermal degradation. We are not concerned with fume formation or processes associated with the minor components.

Each of the minerals can undergo transformation of its own or it can react with other minerals or transformed minerals during combustion. Quartz tends to be very stable thermally. The small grains may form amorphous silica but the large grains retain their crystallinity for the most part. Pyrite, however, can go through a number of transformations depending on temperature, local oxygen potential, time and temperature. The other major mineral group, clays, undergo complex reactions including dehydration, crystallographic transformation, and melting. Carbonate phases such as calcite ($CaCO_3$) and dolomite $(Ca,Mg)CO_3$ undergo decarboxylation (loss of CO_2) to form the corresponding calcined phase. These phases are of course available as sorbent material for the SO_2 and SO_3 present in the combustion gases. The extent of reaction between the calcined phases and the sulfur gases is of course dependent on various factors such as particle size, temperature, pore size, and sulfur concentration gradients.

The organically bound constituents undergo various processes during combustion of the coal. For our purposes during combustion the elements are released into the gas stream. However, they will condense rapidly onto cooler particles. The species are very reactive and oxidize when exposed to oxygen. There is some thermodynamic and experimental studies to show that the sodium forms hydroxide (NaOH) whereas Ca and Mg, for example, form calcium oxide and magnesium oxide. All these phases will tend to react readily once condensed onto cooler particles such as quartz and transformed clay grains. There are also competing reactions between the released species and sulfur oxide moieties. Once again the extent of reaction is dependent on various factors including temperature, size and shape of particles, concentration gradients, and local gas atmosphere.

The complexity of the processes at this stage precludes the development and application of a rigorous accurate model or program to predict the mineral transformations. Researchers are still developing these models. However, to date, the models are based on too little data to be relevant to all coals and combustion conditions. For our purposes we are concerned with the transformations of the coal minerals which directly affect ash deposition. Therefore we have to perform simple experiments to obtain ash species representative of the ash formed in the particular combustion equipment. This experiment may include drop-tube studies, pilot-scale experiments, or if properly designed and performed a laboratory scale experiment.

Based on the authors experience drop-tube experiments are the most practical for this purpose. The drop tube can be designed to simulate conditions coal minerals 'see' in a full-scale combustor. These conditions include, particle residence time, particle time temperature history, gas atmosphere, gas temperature, and particle density. Indeed, drop-tube experiments have been the basis of the development of the approach presented here. The important aspect is that the ash produced in the drop tube, under carefully controlled conditions is adequately sampled and characterized. The sampling can be accomplished by a variety of methods such as a multi-cyclone or cascade impactor.

The characterization of the ash is extremely important. It must be remembered that we have to establish the deposition propensity of the ash from this data. Two methods have been developed to full characterize the ash with respect to the ash deposition processes. If we assume that the ash has been produced in a drop tube and the collection device has classified the ash with respect to size then the remaining task is the determination of the size, shape, and chemistry of the ash particles. The two techniques used are CCSEM and SEMPC.

The CCSEM analysis of the ash produces the same type of results as the CCSEM analysis of the coal. Thus a direct comparison can be made between the coal mineralogy and the species observed in the ash samples. This is important in order to obtain a data base with which relevant models of ash transformations can be obtained. For example, comparison of the data can show that there is significant reaction between the calcite and the cay particles. The size of the various particles produced in the ash is also important with respect to ash deposition as the size and shape of the particles influence the trajectory of the particles at or near tube surfaces. Thus it is possible to establish the effect of coal preparation (grinding, pulverizing, cleaning, etc.) and combustion conditions on the size and mineralogy of the ash particles.

The second technique used is Scanning Electron Microscopy Point Count, SEMPC. This technique was developed specifically to determine the phases and characteristics of ash particles and deposits. Full details of this technique can be found elsewhere (1). The technique provides the following data:

- o Full chemical composition of random points within the sample

- o Average chemical composition of the sample

- o Complete phase analysis including crystalline and amorphous

- o Viscosity and base/acid ratio of amorphous phases

The analysis involves the systematic microprobe analysis of over 240 points within a suitably prepared sample. A complex normative analysis of the quantitative data determines if the chemical composition of each point corresponds to one of over 40 known crystalline phase common to coal, coal ashes, or deposits (based on extensive x-ray diffraction analysis data). Failure to classify the composition amongst the crystalline phases causes the point to be classified as amorphous. The chemical composition of the amorphous phases are used further to obtain a measurement of the viscosity of the various phases. The viscosity is calculated using a method developed by Kalmanovitch and Frank (7). This method calculates the viscosity not only for full coal ash chemical compositions but also for simple silicate phases such as that produced following reaction between silica and sodium. The average chemical composition data produced with this technique is also valuable as the amount of sample produced in the drop tube is too small for standard bulk analysis.

Thus the characterization of the ash provides the data with which to predict the deposition of the ash. In order to accomplish this a model of the processes involved in deposition is required which utilizes the data obtained with respect to the characterization of the coal minerals and the ash species.

ASH DEPOSITION PROCESSES

The deposition of the ash is not a function of the bulk ash chemistry but a matter of probabilities of an ash particle sticking to a surface. There are two types of surface which have to be considered. The first is the bare metal tube. The second is a deposit surface. We have to consider the factors which affect the probability of an ash particle sticking to either surface. Therefore there are two cases, metal and deposit surface. The first case is an initiation step. Without ash particles sticking to the tubes deposits will not grow. The second stage controls the rate of growth of deposits and the formation of the troublesome hard-bonded deposits.

Deposit Initiation:

In this step the approaching particle has a finite probability of sticking to the surface. The factors which affect the probability are:

o   Size, shape and momentum

o   Temperature

o   Amount of liquid phase on the surface of the particle

o   Chemistry of the liquid phase

o   The viscosity and surface tension of the liquid phase

o   Structure and nature of the metal surface

We can envision two extremes. the first is the case where there is no liquid phase present. The probability of sticking will be zero and the collision of the particle will be completely elastic. The other extreme is where the particle is completely molten, the viscosity of the liquid is low, and the metal surface has a surface conducive to adhering to the particle. On contact the particle will deform and interact with the surface. This results in adhesion. Of course the whole range of the scenario takes place. We are dealing with a large number of particles required. For example, to form a dense deposit 10 microns thick and 1" x 1" square requires the impaction and adhesion of over 12,000 10 micron diameter particles. Clearly statistical tools have to be used. There are many ways to accomplish this. The procedure used by the author is as follows:

1. From the CCSEM analysis of the ash sample an estimate is established on the size distribution of the major species. These species will tend to dominate the particle flux impacting the metal surface.

2. The SEMPC data is used to establish the amount of liquid phase available in the sample.

3. Furthermore, the viscosity of the various liquid phases can be calculated. This is done on a particle by particle basis. The data is represented

in the form of population histograms. These histograms are called viscosity distributions. The viscosity is calculated at a given temperature, usually the gas temperature in the region of the surface of the target.

By studying the data one can establish a scale or a relative degree of sticking probability. Figure 1 compares the viscosity distribution of the amorphous phases at 1100 C (2000 F) of two coal ashes. The ash with a high population of low viscosity liquid phases will have a higher propensity to form a deposit on the metal surface than an ash with the bulk of amorphous phases with high viscosities. Of course other factors have to be considered in an overall model such as the relative amount of liquid phases. If the ash only has 10 % liquid phases at a given temperature then clearly the amount of particles which can adhere is greatly reduced no matter what the viscosity of the liquid. Conversely, an ash with 100 % liquid phases will increase the probability of particle sticking at even relatively high viscosities. However, when all the various factors are considered the viscosity of the liquid phases dominates the probability of particle sticking and hence the formation of the initiating layer.

Drop tube deposition studies at the University of North Dakota Energy and Environmental Research Center (4) have shown that the initial deposit layer is formed from particles with low viscosity and diameters within the size range between 10 and 40 microns in diameter. Smaller particles did not participate in the formation of the initial layer. This data indicates the importance of particle size and viscosity in the formation of the initial deposit layer. It can be expected that coals which form ashes with smaller size particles, lower amounts of surface liquid phases and liquid phases with high viscosities will have a low propensity to form an initiating layer. However, we now have to consider what happens after the initiating layer is formed.
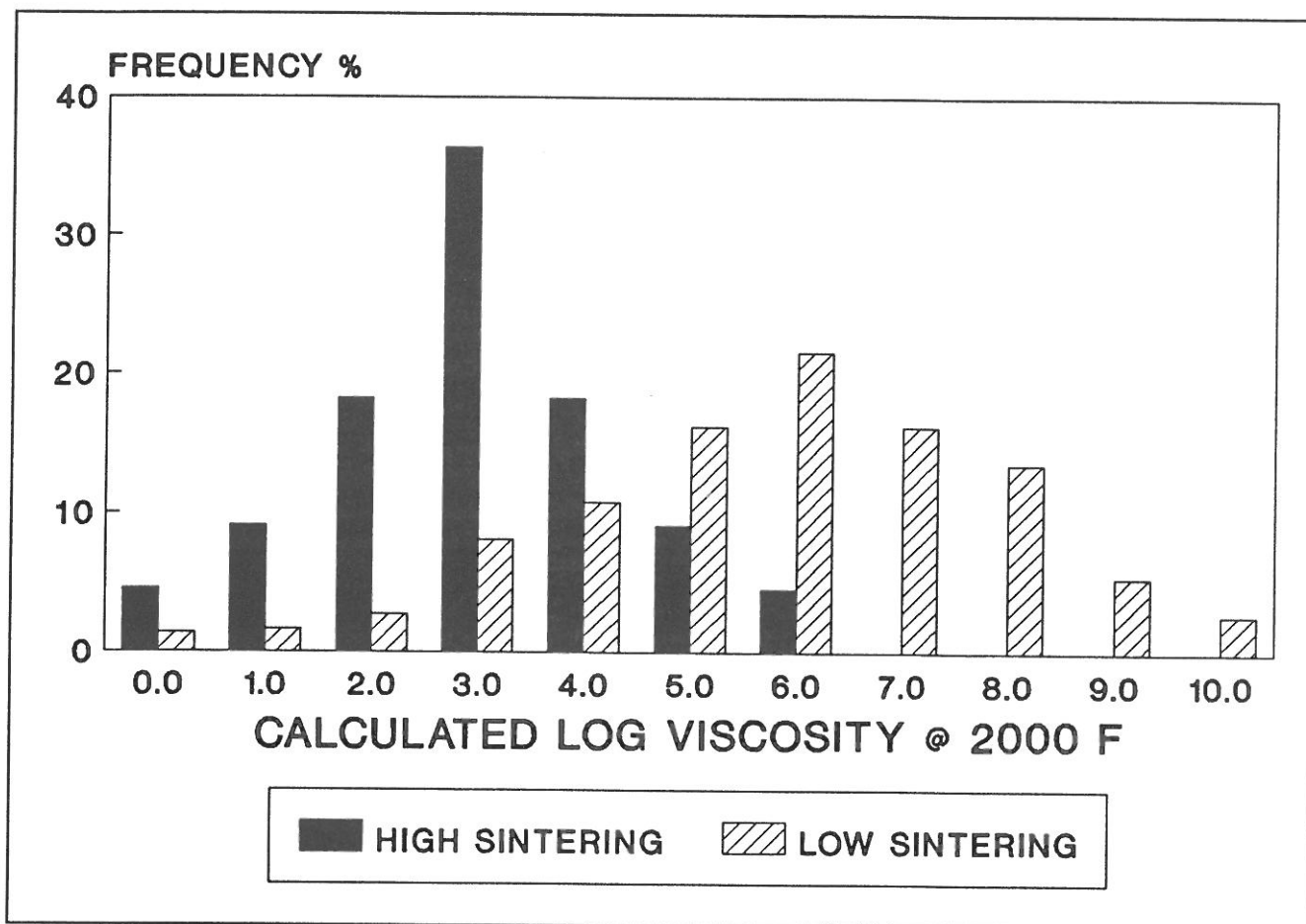
Figure 1. Comparison of viscosity distribution for two coal ashes.

Deposit Growth:

It has to be acknowledged that the formation of a 10-20 micron thick deposit on the surface of the tube will not adversely affect overall performance of a boiler. However, the formation of the deposit is important as it affects the surface that the gas-entrained ash particles impact. The probability of an impacting particle sticking to the surface is now not dependent only on the ash particle itself but the surface characteristics of the deposit in the region of impact must be also considered. Once again we can examine two extremes: the case where the deposit surface acts as an inert phase where only the larger, more fluid particles adhere, or the second case where the surface of the deposit captures all impacting particles. This second case is very important as it removes virtually all variables due to the ash particles. Thus we have factors involved in the deposit itself which affect deposit growth and, to some extent more importantly, development of strength. The development of strength is important as it affects the degree of difficulty of removal. Knowledge of the time needed for a given deposit to form a hard bonded mass on the tube surfaces can be used to establish soot-blowing cycles, load cycling to shed deposits, and other methods. We have to examine the factors which affect deposit growth and development of strength.

An ash deposit is a consolidated mass of fine ash particles. Ash particles, the bulk of which are present below 50 microns in diameter, have collected and sintered to form deposits centimeters or more thick. What are the processes that occur which affect the degree of sintering and hence development of strength and rate of growth. Sintering can be described as the process of consolidating a system with a high surface area to a system with a lower surface area. Raask (8) has related the sintering model of Frenkel (9) to the sintering of coal ash. Simply this model shows that the reduction of pore volume of a packed collection of spheres of known radius with a fixed viscosity is proportional to the surface tension of

the liquid phase and inversely proportional to the viscosity and radius of the particles. Based on this model one can say that at a given temperature the rate of formation of a hard bonded deposit will be greater for a collection of small particles with low viscosity than for a collection of large particles with high viscosity.

While this model has given valuable fundamental insight into the formation of hard-bonded deposits further parameters must be considered. It is essential to remember that the Frenkel model is for packed, relatively homogeneous (both in respect to size and composition/viscosity) particles. The analysis of the ash particles has shown that there is a wide variation in the size, shape and chemical composition of the particles. Furthermore, the Frenkel model does not take into account the fact that chemical reactions can occur between the various phases. Another factor is that as the ash particles are transported to the surface of the deposit by aerodynamic forces and are not manually packed the sintering that occurs will be between random particles. Once again there is the need to look at relevant statistics. That is, what is the probability of two small particles with sufficiently low viscosity and suitable chemistries of liquid phases to be in contact with each other? Conversely, what is the probability of two particles being in close contact and not sintering to any extent?

From CCSEM and SEMPC analysis we know the size distribution of the ash particles, the phase assemblage, viscosity, and chemical composition of the liquid phases on a particle by particle basis. We can use this data to gain some insight into the degree or relative degree of sintering the ash particles will undergo within the deposit. An important aspect is to assess the degree to which the surface of the deposit will become the dominant factor in the rate of growth. This is the probability of an impacting ash particle adhering to the surface becoming more dependent on the target surface. The complex processes involved

must be reviewed with respect to the measurable parameters. If we assume that we are not to correlate the model directly with a full-scale deposit then we can make the assumption that all we will obtain is a relative degree of sintering. Therefore, if we decide on a temperature, for viscosity calculations, we can use the data from CCSEM and SEMPC analysis to obtain a relative degree of sintering. From this we can assess the extent to which a captive liquid phase will form and hence the rate of growth. The latter involves, of course, the assumption that the particle flux approaching the tube does not vary.

We can use the size distribution of the ash particles and the viscosity distributions initially to obtain an idea of the physical nature of the ash particles. That is, are we dealing with large particles of high viscosity, etc? However, the next stage is a bit more complicated. If two particles of equal size, amount of liquid phase, and viscosity are in contact with one another then, according to Raask the sintering will proceed based on the driving force due to the reduction in surface area. However, the two particles may have liquid and solid phases which can react. This reaction, or potential to react, can be a major driving force with respect to the sintering process. We have to establish if the phases present will have the phase assemblage and chemistry which will accelerate the sintering process. The simplest method used is to look at the base-to-acid ratio of the phases, especially the liquid phases. The base-to-acid ratio of silicate systems is widely used in the ceramic and refractory industries as a measure of relative reactivity. Once again the data from the SEMPC is invaluable in this approach. The base-to-acid ratio for each of the liquid phases is calculated and a population density similar to the viscosity distribution is obtained. The distribution is usually multimodal, and the multi-modality indicates the extent to which reactions can occur between the ash particles in a deposit. Indeed, the distributions have been used to establish the degree of homogenization that has occurred within the deposit due to these reactions. This data is then used to

establish the degree of reactivity that can occur between adjacent particles. The greater the degree of reactivity the greater the driving force for reactive liquid phase sintering. Furthermore, the amount, type, and chemistry of the product of reactions can be predicted. This allows further predictions as to rate of deposit growth and development of strength. Of course, factors such as temperature gradients through the deposit, the effect of porosity on these gradients, the change in particle flux with time and shape, and thickness of deposit must also be considered. However, as a indication of the extent to which an ash deposit will continue to sinter in a manner which will facilitate further growth and development of strength the base/acid ratio is very useful.

CONCLUSIONS

A descriptive model of ash deposition has been introduced. This model shows that to properly understand the deposition potential of a coal various key parameters have to be established. These parameters are the size, shape, phase assemblage, chemistry of individual phases, and physical properties of the particles at a given temperature. This data, currently can only be obtained through production of ash in a combustion system, such as a drop-tube furnace, pilot-scale facility etc. This ash must be fully characterized using advanced analytical techniques. Two techniques used at this time are CCSEM and SEMPC. These techniques have been developed specifically to provide the relevant data to understand the deposition behavior of coal ash.

The behavior of ash was separated into two areas, the initiation and the deposit growth. In the initiation step it was shown that the characteristics of the ash particles impacting the metal surface dominate the probability of the particles sticking. In particular the size, chemistry, surface tension and viscosity were identified. In the deposit growth stage it was shown that sintering processes within the deposit are complex. However, an understanding of these complex processes was necessary as it provides an insight into the

extent to which the deposit will grow and develop strength with respect to time and temperature. Another factor with respect to the deposit is how the deposit surface presented to the impacting ash flux changes with time. This is important as the deposit surface can change from having almost negligible influence on the probability of ash particles sticking to dominating influence on particles sticking. The latter case is the so-called captive liquid phase. An understanding of sintering processes is necessary in order to establish the extent of deposit growth and development of strength. In particular, the role of the phase assemblage, the viscosity and the chemistry of liquid phases has to be considered.

In conclusion, the complex nature of ash deposition precludes at this time a simple universal system for predicting the behavior. An understanding of the fundamental processes provides a basis for the development of user-specific methods. These methods have to be based on rigorous analytical data as well as operating parameters such as tube metal temperatures, gas temperatures, combustion stoichiometry, excess air, coal particle size, and other relevant data. The methods can be designed as screening techniques for specific coals, establishing different operating conditions for problem coals, establishing soot-blowing cycles to provide effective cleaning, and establishing the effect of fuel blending/beneficiation on deposition. Of course, a better understanding on the deposition processes can also be used in the design of new units.

ACKNOWLEDGMENTS

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TABLE 1

MAJOR MINERALS IN COAL

Mineral Name	Major Oxide Components
Quartz	SiO_2
Kaolinite	SiO_2, Al_2O_3
Illite	SiO_2, Al_2O_3, K_2O
Montmorillonite	$SiO_2, Al_2O_3, CaO, Na_2O$
Pyrite	Fe_2O_3, SO_3
Calcite	CaO
Dolomite	CaO, MgO
Sodium Carboxylate *	Na_2O
Calcium Carboxylate *	CaO

* - represents organically bound elements (mainly western fuels)

TABLE 2

EXAMPLE OF CCSEM DATA FOR A BITUMINOUS COAL

MINERAL PHASE	PERCENT
QUARTZ	31.0
ALUMINOSILICATE (KAOLINITE)	20.0
K-ALUMINOSILICATE (ILLITE)	1.0
CA-ALUMINOSILICATE (MONTMORILLONITE)	3.0
PYRITE	12.0
CALCITE	6.0
GYPSUM	0.1
UNKNOWN (UNCLASSIFIED)	0.1

SIZE DISTRIBUTION OF MINERAL GRAINS

MINERAL PHASE	SIZE RANGE (MICRONS)					
	≤ 1.2	1.2-2.2	2.2-4.4	4.4-6.0	6.0-11.0	≥ 11.0
QUARTZ	0.4	2.7	8.5	3.1	4.0	25.0
KAOLINITE	0.3	2.0	4.6	2.0	2.5	2.0
ILLITE	0.0	0.2	0.3	0.1	0.0	0.0
MONTMORILLONITE	0.0	0.1	0.5	0.2	0.0	1.0
PYRITE	0.2	1.0	1.2	1.8	0.2	4.0
CALCITE	0.1	0.4	3.0	0.0	0.0	0.0
GYPSUM	0.1	0.2	0.1	0.0	0.0	0.0
UNKNOWN	0.3	0.1	0.0	0.0	0.0	0.0